The Role of Asphaltenes, Resins and Other Solids in the Stabilization of Water in Oil Emulsions and its Effect on Oil Production in Saudi Oil Fields

by

Mohammad Hassan Alqam

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

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This thesis, written by Mr. Mohammad Hassan Alqam under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CHEMISTRY.

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Dedicated

to

my parents, Brothers, sisters, wife and my

Children

Acknowledgment

First and foremost, all praise to Allah, the Almighty, for giving me the courage, strength, and patience to complete this work.

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ملخص الرسالة

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التخصص: كيمياء

سنة التخرج: يونيو ١٩٩٧

أدى تكون المستحلبات الثابته خلال انتاج النفط , في بعـــض الحقـــول العـــائدة لشـــركه ارامكـــو السعوديه, الى زيادة كبيرة في استخدام مواد كيميائيه كثيره بالاضافه الى خسارة في انتاج النفط.

لقد اظهرت النتائج ان المواد الصلبة ساهمت في ثبات المستحلبات. لقد تم فصل المواد الصلبة من عدة عينات من المستحلبات وتم تحليل مكوناتها مستخدما جهاز انعطاف اشـــعة اكـــس والتحليـــل بالقياس الوزني الحراري وقياس الحرارة بالمسح التفاضلي. واظهرت المعلومات ان المواد الصلبة تتكون من كربونات الكالسيوم البلورية, الشمع, مركبات اسفلتية ومركبات راتينجية.

كدلك تمت أعمال اضافية على تلك المواد لتميز بينها. لقد تم استخدام مقياس ضغط البخار لتحديـــد معدل الوزن الجزئي لهدة المواد (الاسفلت\الراتينج و الشمع) كدلك تم اجراء دراسة على الشـــــمع المفصول من المستحلبات باستخدام جهاز محاكاة التقطير.

لقد اظهرت النتائج ان المواد الشمعية التي تؤدي الى ثبات المستحلبات هي مواد دقيقة التبلور فـــي طبيعتها. ودلت الدراسة كدلك على ان المواد الشمعية بالاضافة الى جزئيات كربونـــات الكالســـيوم البلورية امتزت المواد القطبية (الاسفلت\ الراتينج) هده العملية أدت الى تغير في قابلية الابتـــلال لبلورات الشمع سامحا لها في الارتحال الى سطح التقاء الماء مع الزيت.مما يســـاعد فـــي ثبـــات المستحلبات.

ماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران

يونيو ١٩٩٧

THESIS ABSTRACT

NAME OF STUDENT : MOHAMMAD HASSAN ALQAM

TITLE OF STUDY : ROLE OF ASPHALTENE, RESIN AND OTHER SOLIDS IN THE STABILIZATION OF WATER IN OIL EMULSION AND ITS EFFECT ON OIL PRODUCTION IN SAUDI OIL FIELDS.

MAJOR FIELD : CHEMISTRY

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Formation of tight emulsions during oil production, in Saudi Aramco's oil fields, has caused a significant increase in demulsifier usage as well as production losses.

Our investigation indicated that these tight emulsions are stabilized by solid materials. These solids were separated from various emulsion samples and were analyzed for their composition using various methods such asX-ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetery (DSC). These data indicate that these solids consist of calcite, wax, asphlatene and resins.

Additional work was conducted to further characterize these material. Vapor Pressure Osometry (VPO) was used to determine average molecular weight of those organic material (asphaltene/resin and wax) . Simulated distillation of wax samples separated from emulsion sample were also carried out. The results of these investigations indicate that the emulsion stabilizing wax material is microcrystalline in nature. These wax crystals as well as Calcite particles adsorb polar fractions of oil (asphaltene/resin). This process alters the wetabillity of these crystals allowing them to be migrated to oil water interface and contribute to emulsion stability.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Oil produced varies form Arab Heavy (API 27 °) through to Arab super light (API 51°). This thesis discuss the emulsion encountered during the production of Arab light (AL- 31 - 33°). A crude oil reservoir contains a mixture of water, oil, and gas trapped in the small pore space of the reservoir rock. Due to the hydrostatic pressure, these fluids are held under considerable pressure in the reservoir. The developed pressure forces the oil out through the production wells and creates significant energy to mix the fluid to form emulsion. The resulting emulsion is simply a combination of the petroleum oil and any associated water and gas in the reservoir. Naturally occurring stabilizing agents (inorganic solids) are usually present in sufficient quantities to stabilize the emulsion. The turbulent flow of the oil-water mixtures through the well casing, valves and chokes produce the necessary energy for emulsification. Once an emulsion forms, it may remain loose and

be relatively easy to treat or it may turn into a tight and difficult- to- treat emulsion.

In most crude oils, solids such as iron sulfide, silt, clay, drilling mud solids and paraffin complicate the demulsification process [1]. To achieve a satisfactory treatment these solids must be removed from the interface. They can either be dispersed in the oil or water. However, the adsorption of asphaltenes and resins from crude oil onto fine solid particles can dramatically alter the wettability characteristics of these solids, thus enabling them to stabilize water-in-oil (w/o) emulsions.

The composition of the formation water can also be an important factor in the stabilization of crude oil emulsions. With divalent ions like Ca^{2+} and Mg^{2+} present , water may form soaps with organic acids of the oil phase (e.g. naphtenic acid). These soaps form mobile films on the interface of oil and water and this will slow down the separation of the two phases. Therefore any chemical process which can eliminate, alter or neutralize these layers will assist oil-water phases separation[2] and speed up the demulsification process. Also, sometimes the use of chemicals may also increase the interaction between droplets and can improve the coalescence process. The

adverse effects [3] of higher concentrations of chemicals as well as the economics favor the use of demulsifying agents at low concentrations.

Emulsions are one of the many problems which are associated with oil production. These emulsions must be resolved satisfactorily to be able to market the produced oil. The nature of these emulsions varies from one crude to another. This is mainly due to the fact that crude oils differ in their chemical composition such as their asphaltenes and other polar molecules contents, associated impurities such as clays and other fine particles as well as their geological history [4,5].

Chemical and physical properties of produced water has also an important effect on characteristic of produced emulsions, which also differ from one reservoir to another and will also change during the life of the reservoir [6,7]. Preliminary investigation indicates that in Saudi Aramco's produced emulsion both composition of oil as well as the chemistry of produced water are responsible for the stability of these emulsion. Therefore, an understanding of the formation of organic solids such as asphaltenes and inorganic solids such as scale products, and pressure and temperature related to the formation of these products, will produce effective methods which can be applied to break tight emulsions. Tight emulsions produced from some

wells in Saudi Aramco's field are creating operational problems in surface facilities. The problem becomes more acute in the winter when the produced fluids cool down quickly causing significant difficulties for smooth operation of the Gas Oil Separation Plant (GOSP). The problem caused by tight emulsions include: (a) increase of pumping cost, (b) erosion of pipeline and equipment due to two-phase flow, (c) increase in corrosion rate and scaling due to the salt content in the formation water (d) lowering of the oil API gravity. Emulsion treatment is expensive. Besides chemical control, other methods of treating emulsion include heating, electrical dehydration and gravity settling. All these are aimed at reducing the bulk viscosity of the continuos phase, increasing the gravity differential of liquids and particles, rupturing the interfacial film by lowering the interfacial tension and neutralizing the electrostatic charges on particles.

1.2 OBJECTIVE

The objective is to investigate the effect of inorganic solids such as (calcite and other fine materials), and organic matter such as (asphaltenes, resins etc.) on emulsion formation and emulsion stability in some Saudi crudes which are creating problem in surface facilities. The study will investigate various methods that will speed up the demulsification process of produced w/o emulsions.

1.3 PRESENT STATUS

An emulsion is a combination of two liquids that are immiscible. One of the liquids is dispersed as droplets in a second immiscible liquid, usually in the presence of an emulsifying agent. In the oil field, the two basic types of emulsions are water-in-oil (w/o) and oil-in-water (o/w). More than 95% of the crude-oil emulsion formed in the oil field are of the w/o type. An emulsion may be tight (difficult to break) or loose (easy to break). Whether an emulsion is tight or loose depends on a number of factors, four of which are (a) The properties of oil and water (b) The amount of agitation, or shear, it undergoes (c) The percentage of oil and water found in the emulsion; and (d) The types and amount of emulsifiers present. Furthermore, petroleum emulsions vary from one oil field to another simply because crude oil differ according to geological age, chemical composition, and associated impurities.

The stability of a w/o emulsion depends on several factors: The emulsifying agent, viscosity, specific gravity, water percentage, age of emulsion, and the amount of agitation. Rheological properties of the crude oil-water interface have been determined by Mohammad et. al. [7]. The effect of temperature and the pressure with demulsification chemicals on the visco-elastic film formed from Buchan crude oil and water have been studied.

The viscous interfacial film formed between crude oil and water, which builds up with time due to further adsorption and rearrangement of indigenous materials present in the crude oils, are believed to contribute substantially to the stability of w/o emulsions.

The presence of an adsorbed layer of asphaltenes from crude oil on finely divided solids were found to alter the wettability and characteristics of these solids dramatically, thus enabling them to stabilize w/o emulsions [8]. The asphaltene-particle and particle-fluid interaction have also been discussed in a paper by Menon et. al. [9]. In this study attempts were made to decrease the stability of w/o emulsions by modifying the surface properties of the solids. The hydrophobicity of the solid particles was attributed to asphaltene adsorption on to the solid surface. The stability of w/o emulsion was decreased either by decreasing the asphaltene adsorption or by changing the fluid-particle interaction through the use of surfactant or pH-adjusted water.

In a recent study Gonzalez et. al. [10] have shown that asphaltenes play an important role in the stabilization of w/o emulsions. They observed that asphaltenes show a moderate capacity to reduce o/w interfacial tension and stabilize emulsions. However, in the presence of other surfactants and fine

particles, asphaltenes enhance emulsion formation. At the solid/ solution interface, asphaltenes adsorb up to a saturation value of 2 to 3 mg/g and modify the mineral wettability. At the oil/ gas interface, the asphaltic fractions adsorb as simple molecules or as liquid crystalline phase, causing foaming problems [10].

More recently Al-Jaziri [11] has investigated various physical factors affecting the stability of w/o emulsions in oil production. He used a specially designed laboratory system to simulate various aspects of emulsion flow in the field. Using this system he examined the effectiveness of various demulsifying chemicals as well as the combined effect of temperature and demulsifiers on breaking emulsions.

PROPOSED WORK

The proposed work consists of a laboratory investigation into various factors affecting the stability of emulsions in some Saudi crude which are considered to be undesirable for a number of reasons, including both upstream and down-stream operation in the petroleum industry.

PROPOSED WORK PLAN

1. Literature survey.

2. Collection of a number of sample from GOSP, problem wells, and non-problem wells for a comparative study.

3. Each well head fluid sample will be analyzed for the following:

- Types of emulsion
- Physical properties of separated oil (viscosity and gravity)
- Chemical composition of oils for asphaltenes and resins.
- Correlation study on oils for resin to asphaltene ratio(R/A) and emulsion stability.
- Total solid contents of emulsion samples.
- Solid composition by XRD, TGA/DSC, FTIR etc.
- Effect of calcium carbonate formation on emulsion stability.
- Comparison of solids produced from tight emulsions with that of loose emulsions.
- Suggest possible physical and chemical ways of minimizing the formation of possible organic and inorganic solids promoters for tight emulsions.
- Analyze brine samples obtained with the oil for conductivity and TDS and correlate the data to emulsion stability.

4. Recommendation for avoiding and breaking of produced emulsions at process-stream.

CHAPTER 2

LITERATURE SURVEY

An attempt to characterize the interfacial film was carried out by Denekas et. al.[12]. They observed that 12.5% of the film was aliphatic hydrocarbon. The presence of inorganic metals at the interface was reported by Dodd et. al [13]. A Study was carried out by Stassner[14] to elucidate the inter-relationship between polar materials and film characteristics. They discovered that the presence of asphaltene material plays a significant role in the stability of the emulsion. Another study reported that the existence of asphaltene in crude oil will alter the wettabillity of fine particles from water wet into oil wet. This alteration of the wettabillity will stabilize the water-in-oil emulsion. Gonzalez et el.[10] investigated the adsorption of asphaltenes and its effect in oil production.

Ramsden[15] reported that solid particles, present in crude oil-water emulsion, have strong ability to stabilize water-in-oil emulsions.

2.1 Stability of Interfacial Film In W/O Emulsion:

The stability of emulsion depends on the hydrophile-lipophile balance(HLB) of the emulsifier. The HLB determines whether an emulsifier will stabilize water-in-oil (w/o) emulsions or oil-in-water (o/w) emulsions. The HLB scale varies from 0-20. Low HLB (<4) implies that less fraction of the emulsifier is soluble in water and thus stabilize w/o emulsion. High HLP (>10) implies that a larger fraction of the emulusifier is soluble in water and thus stabilize oil-in-water emulsion (reverse emulsion).

Generally, Produced oil-field emulsions are stabilized by films that form around the water droplets at the oil-water interfaces. It is believed that the oil-water interface is stabilized by asphaltene and resin fractions. These films are believed to result from the adsorption of high molecular weight polar molecules that are interfacially active (surfactant-like material). These films complicate the demulsification process by increasing the interfacial viscosity as well as reducing the interfacial tension. The demulsification process will also slowdown due to the formation of highly viscous interfacial films around the water droplet. This will prevent the coagulation of water droplets and this will delay the demulsification process.

The characteristics of the interfacial film are a function of the crude oil type (asphaltenes, and paraffines composition), pH of water, temperature,

extent to which the adsorbed film is compressed, aging time and concentration of polar molecules in the crude oils [14,15,19&20]. A good correlation exists between the occurrence of incompressible interfacial film and emulsion stability. These films are classified into two categories based on their mobilities[14,15].

These are like an insoluble skin on water droplets and are characterized by very high interfacial viscosity. There is a considerable evidence that these films are formed by polar fractions of the oil, other emulsifiers and may be further stabilized by fine solids. These films play an important role in hampering the drop coalescence process. They provide a structural barrier to droplet coalescence and increase emulsion stability. These films also have viscoelastic properties.

2.2 Factors Affecting Stability of Emulsions

There are several parameters that play a significant role in the stability of the interfacial films. These important factors are:

- Heavy polar fraction in the crude oil.
- Solids including organic (asphaltenes, waxes, etc) and inorganic(clays, scale, corrosion products, etc).
- Temperature.

- Drop size and drop size distribution.
- pH of the brine.
- Brine composition.

2.2.1 Heavy Polar Fraction In Crude Oil

It is well established that the indigenous stabilizers are of higher molecular weight polar fraction of the crude oils [14,15,21-24]. These are mostly asphaltene and resins and oil soluble organic acids (e.g. naphthenic, carboxylic acids) and bases. It is found that these compounds are the main constituents of the interfacial film surrounding the water droplet that give emulsions their stability.

2.2.1.1 Asphaltenes and Resins

Asphaltenes are simply n-alkane insoluble fraction of the vacuum residue obtained from crude oil during refining. Asphaltenes are dark brown to black friable solids with no definite melting point. The chemical structure of asphlatenes is extremely complicated, and isolation and identification of individual asphaltene molecules has not been proven possible.

Asphaltene do, however, possess several common chemical and geometric characteristics. All asphaltenes are primary composed of carbon, hydrogen, oxygen, nitrogen and sulfur. In general, asphaltene are believed to

be polynucler aromatic ring systems bearing alkyl side chains. The condensed ring systems vary in size from 6 to 20 rings and alkyl chain lengths between 4 and 20 carbon atoms. The apparent high molecular weight of asphaltenes (2000-10000) is attributed to the linking together of the aromatic sheets with alkyl chains[25].

Another common property of asphaltene is their tendency to associate in solution. This tendency has been regarded as a key factor hindering the conversion of heavy vacuum residue into more valuable lighter products. In addition, this self-association has led to uncertainty in the determination of the molecular weight of asphaltenes. Techniques using an ultracentrifuge give asphaltene molecular weight up to 300,000 [25], whereas the osmotic pressure method gives molecular weights up to 80,000[25]. Even lower molecular weights (1000-5000) are obtained using vapor pressure osmometry[25]. These discrepancies can likely be attributed to the varying degrees of asphaltene aggregation that occur during these different weight determinations. Attempts to understand asphaltene self-association have been the subject of several studies [26-29]. It has been shown [30] that asphaltenes exist in the oil as colloidal suspension, and are stabilized by resins adsorbed on their surface.

Resins have the tendency to solubilize asphaltene and to form micelles. The polar head of resins are attracted to polar functional groups such as carbonyl, carboxylic, amine and amides.

Asphaltenes are considered as good emulsifier due to its behavior as surface active materials. Surfactant is a molecule containing both polar and non-polar parts (amphiphilic). These molecules sit at the interface because the polar portion is attracted to the polar medium, which is water in water-in-oil emulsion, and the non-polar to non-polar medium which is the oil.

Asphaltenes , and other indigenous materials in the crude, adsorb at the water droplets interface and form rigid skin around the water droplets. This action will complicate the coalescence of water droplets and will induce emulsion stability. So, The adsorption of asphaltenes at water-oil interface will retard the drainage of the film 'rigid skin'. The main mechanism involved in this retardation is the steric repulsion or hindrance caused by the high molecular weight materials in the film. The asphaltenes are surrounded by the polar head groups of the resins while the nonpolar alkyl group tails interact with the oil phase.

It has been suggested that the asphaltenes tend to aggregate into micelles which have an adsorbed layers of aromatic resins as a stabilizing agents [31-33]. Researchers also established that asphaltenes dissolved in the

oil phase in the form of a molecular dispersion, have no significance for emulsion stabilization of crude oils, when compared with stabilization by colloidally-dispersed asphaltenes [34-37]. It was further determined that asphaltenes only stabilize water-in-oil emulsions if they are near or above the point of incipient flocculation which suggest that their mode of action is to collect at the interface in the form of finely divided solid particles [38-40]. From these studies, it can be concluded that bringing the asphaltenes in a better-dissolved state decreases their emulsion stabilizing power. The asphaltene precipitation is strongly influenced by the interaction between asphaltenes and other components of the oil. Asphaltenes most commonly occur in the form of colloidal dispersions, however, they tend to cluster into aggregates [41]. Various naturally occurring polar molecules and surface active materials indigenous to crude oil (such as asphaltenes, resins, porphyrin complexes, paraffin particles, clay, and sand) [42] as well as some other polar molecules which are produced as a result of the recovery methods applied in oil production (such as fire flooding) can adsorb at oil-water interface and act as chemical emulsifying agents which stabilize water-in-oil emulsions. Recent studies indicates that resins have a strong tendency to associates with asphaltenes. The aggregates play a key role in the stabilization of asphaltenes in the crude oil [34,43-44]. This phenomenon

was originally described by a colloidal model [45] where asphaltene aggregates were assumed to be kept in solution by a layer of resin molecules. This was later refined to an asphaltene resin interaction model [34, 46-49].

RESINS:

Resins are complex high molecular weight compounds that are not soluble in ethylacetate but soluble in n-heptane. They are also hetrocompounds like asphaltenes and contain oxygen, nitrogen, and sulfur atoms in their molecules. Molecular weights of resins range from 500 to 2000. Resins have a strong tendency to associate with asphaltenes and together they form a micelles. Bobra[22] investigated the effect of resins on emulsion stability. They found out that both resins and asphaltens can act as effective emulsifier.

2.2.2 SOLIDS

It is well known for a long time that finely divided solids are capable of stabilizing emulsions [48,49]. It is also established that solids only act as emulsifying agents when surface active agents adsorb onto their surfaces. The effectiveness of these solids in stabilizing emulsions depends on factors such as particle size, inter-particle interaction and the wettability of the solids[17,20]. Solids particles stabilize emulsions by diffusing to the oil-water interface where they form rigid structure (skin) that can sterically

prevent the coalescence of emulsion droplets. Furthermore, solid particles at the interface may be charged which may also enhance the stability of the emulsion. Particles must be much smaller than the size of the emulsion droplets to act as emulsion stabilizers. Typically these solid particles are sub-micron to a few microns in size.

Depending on their wettability, **which is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids and wettability is expressed in terms of the contact angle,** they would stabilize oil-in-water emulsions or water-in-oil emulsions, for instance hydrophobic particles would stabilize water droplets, where as hydrophilic particles would stabilize oil droplets. The three phase contact angle can be used to predict the type and stability of solids-stabilized emulsions [50, 35]. In addition, as indicated in the literature, the particle size of the solids is also important as it determines the equilibrium position of a particle at an interface [51,52].

2.2.2.1 THE INFLUENCE OF WAX ON CRUDE OIL EMULSION STABILITY

The majority of crude oils and crude oil products contain substantial amounts of petroleum wax. Depending on the kind of oil, the composition of the wax range from predominantly low molecular weight n-alkanes (C20-

C40) to high proportions of high molecular weight isoalkanes and cyclic alkanes [53]. The former type of wax is termed paraffin or distillate wax and generally crystallizes as large needles and plates while the latter type is termed as microcrystalline or amorphous wax.

The role of wax in stabilizing emulsions has been demonstrated [54,55]. These researchers have shown that emulsions were significantly more stable with small crystals than with large ones which is consistent with solid stabilization of the oil/water interface.

2.2.3 TEMPERATURE

Temperature can affect emulsion stability significantly. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubilities in the oil and water phases. These in turn affect the stability of the emulsion. The most significant effect of temperature is on the viscosity of emulsion: it decreases with increasing temperatures. This decrease is mainly due to a decrease in the oil viscosity. When waxes are present (crude below its cloud point) and are the source of emulsion problems, application of heat can eliminate the emulsion problem completely by redissolving the waxes into crude oil. Temperature increases the thermal energy of the droplets and hence increases the frequency of drop collisions. It also reduces the

interfacial viscosity and this results in a faster film drainage rate and enhances drop coalescence.

Effect of temperature on interfacial films was studied in some detail by Jones et al.[15]. It was shown that an increase in temperature led to a gradual destabilization of the crude oil/water interfacial films. However, even at higher temperatures, a kinetic barrier to drop coalescence still exists. Temperature influences the rate of build-up of interfacial films by changes in the adsorption rate and characteristics of the interface. It also influences the film compressibility by changes in the solubility of the crude oil surfactants in the bulk phase. Slow degassing (removal of light ends from the crude oil) and aging leads to significant changes in the interfacial film behavior at high temperatures. The films generated by this process remain incompressible and non-relaxing (solid film) at high temperatures and emulsion resolution is not affected by heating.

2.2.4 DROP SIZE

Generally, emulsions have a droplet size distribution rather than a fixed droplet size. Droplet size distribution is normally represented by a histogram or by a distribution function of some sort.

Generally emulsions that have smaller droplets will be more stable. For water separation, drops have to coalesce and the smaller the drops, the longer it will

take to separate. The droplet size distribution affects emulsion viscosity: it is higher when droplets are smaller. Emulsion viscosity will also be higher when the droplet size narrow.

2.2.5 pH

pH of the water has a strong influence on emulsion stability [14,15,21]. The stabilizing, rigid emulsion film contain organic acids and bases, asphaltenes with ionizable groups, and solids. Adding inorganic acids and bases strongly influence their ionization in the interfacial films and radically changes the physical properties of the films. The pH of the water affects the rigidity of the interfacial films. It was reported [14] that interfacial films formed by asphaltenes are strongest in acidic pH and become progressively weaker as the pH is increased. In alkaline medium the films become very weak or are converted to mobile films. The films formed by resins are strongest in base and weakest in acid medium and the films formed by wax-oil fraction are insignificant. Solids in the emulsions can be made oil-wet by asphaltenes and this effect is stronger in an acidic than in a basic medium. These partially oil-wet solids tend to stabilize water-in-oil emulsions.

pH influences the type of emulsion formed. Acid or low pH generally produces w/o emulsions whereas basic or high pH produces o/w emulsion.

Optimum pH for demulsification is around 10 without demulsifier. Addition of a demulsifier enhances demulsification after one hour and almost complete water separation is achieved after 24 hours over a wide range of pH.

Brine composition also has an important effect (in relation to pH) on emulsion stability. Optimum pH (for water separation) changes from approximately 10 for distilled water, to between 6-7 for the brine solution. This is due to ionization effect (association/interaction of ions present in the brine with the asphaltene). A study conducted on Venezuelan crude[14] suggests that for most crude oil-brine systems, there exists an optimum pH range for which the interfacial film exhibits minimum emulsion stabilizing, or maximum emulsion breaking properties. The optimum pH for maximum emulsion stability depends on both the crude oil and brine composition. The latter seems to be more important.

Frequently, severe emulsions upsets occur in surface treating facilities following acid stimulation [19, 56,57]. In many cases it has been linked to formation damage as well. Following acid treatment, the wells are very slow to clean up and often result in partial or complete plugging of the well. This plugging and formation damage generally occurs due to solid precipitates, or sludge, being formed on contact of the crude oil with the acid. These precipitates are mainly asphaltenes, resins and other high molecular weight

hydrocarbons. These materials are apparently precipitated from the crude oil by the reduction in pH as a result of acid contact[57]. While the sludge formed during an acid treatment are extremely difficult to treat (due to high concentration of precipitated asphaltenes), there is a link with the emulsion problem. It is an extreme case of the effect of pH on emulsion stability. These are among the most tight emulsions produced. Proper design of the acid treatments necessary to avoid well productivity decline and emulsion upsets due to acidization[56]

2.2.6 Brine Composition

Specific ions present in the brine also influence interfacial film behavior. Effect of brine composition on interfacial film (and emulsion) stability was reported [15]. Water from petroleum formation generally contain a complex mixture of ions. Sodium and chloride ions are usually present in high concentrations while other ions are present in wide range quantities. At the interface, these ions may react chemically with the hydrophilic groups to form insoluble salts. In the studies[14,15,21], an insufficient number and variety of crude oils-brine systems were tested to draw any concrete conclusions regarding the effect of brine and oil composition on interfacial film and emulsion stabilizing properties.

2.3. Emulsifier

Produced oil-field emulsion can be stabilized by a wide range of emulsifiers. These emulsifier include:

- Finely-divided solids: these can act as stabilizing solids such as drilling mud (Colloidal clay), produced sand, iron sulfide from pipe corrosion, precipitated minerals due to scale formation. The effectiveness of these solids in stabilizing emulsions depends on a number of factors such as particle size, inter-particle interactions, and the wettability of the particles.
- Surface active agents or surfactant; surfactant in the crude oil such as naphthenic acid, injected for corrosion or wax deposition control. These emulsifier are amphiphatic compounds that are partly soluble in both water and oil. They have a hydrophobic part that has an affinity for the oil and a hydrophilic part that has an affinity for water. These emulsifier concentrate at the oil-water interface where they increase the interfacial tension and prevent coalescence of the dispersed droplets. Emulsifier also induce electrical charges on the droplets causing them

to repel each other. Thus, the stability of an emulsion depends on the physico-chemical characteristics of the emulsifier.

2.4. DEMULSIFICATION:

Demulsification is the process of breaking a crude oil emulsion into water and oil and this takes place at the water-oil interface. An effective deumulsifier must have two aspects of demulsification: (a) The speed at which this separation takes place (b) the amount of water left in the crude oil after separation.

A fast rate of separation takes place and low value of the residual water in the crude oil are what the oil producer interested in. Produced oil generally has to meet company and pipeline specification. In Saudi Aramco, the oil shipped from Gas Oil Separation Plant (GOSP) may not contain more than 0.2% basic sediment and water(BS&W) and 10 PTB(pound of salt per thousand barrels of crude oil). This low value of BS&W and salt content is required in order to reduce corrosion and deposition of salts. In refinery operations the primary concern is to remove inorganic salts from the crude oil before they cause corrosion or other detrimental effects in refinery equipment. The salts are removed by washing the crude oil with relatively fresh water.

2.4.1. DESTABLIZING EMULSIONS

Produced oil-field emulsions possess a degree of kinetic stability. This stability arises from the formation of interfacial film encapsulating the water droplets. To separate this emulsion into oil and water, the interfacial film has to be ruptured and the droplets made to coalesce. Therefore, destabilizing or breaking emulsions is linked very intimately to the removal of this interfacial film. The factors that enhance or speed demusification process will be discussed here.

2.4.1.1. TEMPERATURE

The application of heat promote both demulsification and treatment process. An increase in temperature:

- Reduce the viscosity of the oil
- Increase the mobility of the water droplets
- Increase droplet collisions and favors coalescence
- Weakens or ruptures the film on water droplets due to water expansion and enhance film drainage and coalescence
- Increase the difference in densities of the fluids which further enhance water settling time and separation.

All these factors favor emulsion destabilization and oil and water separation. However, heat by itself is not a cure at all and has some limitation e.g loss of light ends from the crude oil. An economic analysis will have to be performed taking into consideration higher heating costs, reduced treating time, residual water in the crude, etc.

An increase in temperature can also be achieved by burying crude oil pipelines or by insulating them: these factors should be carefully evaluated during development especially where there is an anticipation of emulsion problems

2.4.1.2. AGITATION OR SHEAR

Generally speaking, reducing agitation or shear will reduce emulsion stability. Very high shear is detrimental and should be avoided. High shear causes mixing of oil and water and leads to a smaller drop size distribution of water droplets in the emulsion. Smaller droplets are relatively more stable than larger droplets. Therefore measure that increase shearing of the crude (for example, chokes, valves, flow obstructions, pressure drops, etc) should be avoided, or at least, reduced. However this is not always possible. (It should be noted that a certain amount of shear is required for mixing the chemical demulsifier).

2.4.1.3. RESIDENCE OR RETENTION TIME

The period of time that the emulsion is held at the treating temperature is the residence or retention. Typically this is a bout 20-30 minutes for normal crude oil production. However it can be much longer for effectively breaking tight emulsions. An increase in residence time increase the separation efficiency and reduces the residual amount of water in the crude. Increasing residence time, however, comes at the expense of high separator equipment cost.

2.4.1.4. SOLID REMOVAL

As previously mentioned, solids have a strong tendency to stabilize emulsions especially if they are present as fines and when they are wetted by both the oil and water. Sometimes removing the solids or their source is all that is required for eliminating or reducing the emulsion problem. Oil-wet solids stabilize w/o emulsions. Water-wet solids can also be made oil-wet by a coating of heavy polar materials and can effectively participate in the stabilization of w/o emulsions. Presence of solid asphaltenes and waxes have a definite detrimental effect on the emulsion problem and every effort should be made to eliminate their presence in the crude oil. The solids can be

removed by dispersing them into the oil or can be water-wetted and removed with the water.

2.4.1.5. CONTROL OF EMULSIFYING AGENTS

Since emulsifying agent are necessarily involved in the stabilization of emulsions, controlling them allows for their destabilization and resolution. Some of the ways to control emulsifying agents include careful selection of chemicals that are injected during oil production. For example, acids and additive during acidization, corrosion inhibitors for corrosion protection, surfactants and dispersants for organic and inorganic deposition control, polymers and blocking agents for water production control, etc.

2.5. MECHANISMS INVOLVED IN DEMULSIFICATION

Demulsification is the separation of an emulsion into its components phases. It is a two step process. The first step is flocculation (or aggregation, or agglomeration or coagulation). The second step is coalescence. Either of these steps can be the rate determining step in the emulsion breaking process.

2.5.1. FLOCCULATION OR AGGREGATION

The first step in the demulsification process is the flocculation of water droplets. During flocculation the droplets clump together forming aggregates. The droplets are close to each other , even touching a certain

points, but may not loose their identity i.e they may not coalesce. Coalescence at this stage only takes place if the emulsifier film surrounding the water droplets is very weak. The rate of flocculation depends on:

- Water content in the emulsion: rate of flocculation is higher when the water cut is higher.
- Temperature of the emulsion is high:- temperature increases the thermal energy of the droplets and make collision more probable.
- Viscosity of the oil is low:- this increase the settling rate.
- Density difference between oil and water is high- this increases the sedimentation rate.
- An electrostatic field is applied:- this increases the movement of droplets towards the electrodes where they aggregate.

2.5.2. COALESCENCE

Coalescence is the second step in the demulsification process and follows flocculation. During coalescence water droplets fuse or coalesce together to form a larger drop. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete demulsification. Coalescence is enhanced by

- High rate of flocculation: increases the collision frequency between droplets

- The absence of mechanically strong film that stabilize emulsions
- High interfacial tensions: the system tries to reduce its interfacial free energy by coalescence
- Low oil viscosity: increases the rates of sedimentation and coalescence
- Low interfacial viscosity- enhance film drainage and drop coalescence.
- Chemical demulsifier: they convert fine solids to mobile soap film which are weak and can be easily ruptured promoting coalescence

CHAPTER 3

EXPERIMENTAL

3.1. EMULSION SAMPLES

Two sets of experiments were performed to characterize the emulsion. In each case representative samples of water-in-oil emulsions were obtained form well heads of different oil fields in Eastern Part of Saudi Arabia. Samples were obtained upstream of chemical injection facilities and are, therefore, considered demulsifier-free. Each emulsion sample was allowed to remain at atmospheric conditions for at least two days before use, to allow time for degassing and enable free water and sediments to settle out.

The Emulsion sample used through this study were obtained from three GOSPs (A,B&C) and four wells (A,B,C &D) from a field in Eastern part of Saudi Arabia.

SAMPLING: A primary concern during emulsion sampling is to minimize shear produced. For this reason flash sampling, where gas evolution and sample valve restriction cause high shear, are not appropriate. A pressure

sampling technique was therefore developed. Details of equipment and procedure are shown in Figure (1).

Pressure samples were collected from three GOSPs (A,B&C)

- Two samples were collected from GOSP A and these samples were taken from upstream of the choke which is fully open (172/64")
- Two samples were collected from GOSP B downstream of the choke which is half open (80/64")
- Two samples from GOSP C down stream of the choke which is quarter open (36/64")

The pressure sampling technique, mentioned above, was used for sample collection.

Eight samples were collected for the four wells mentioned above under the same conditions as GOSPs samples.

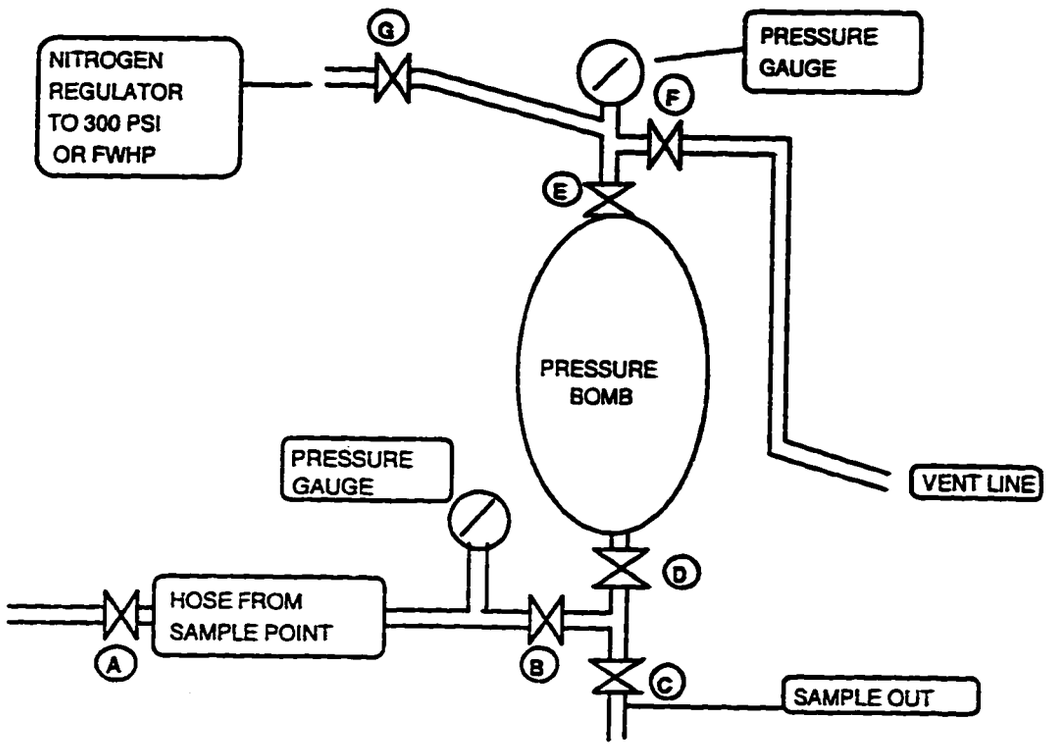


Figure 1. Schematic diagram of equipment used for emulsion sampling.

CRUDE OIL

The emulsion samples allowed to stand at atmospheric pressure for at least a day, this will cause the emulsion to be partially separated into oil layer at the top and water layer at the bottom. This kind of separation is due to gravity.

WATER

The composition of water separated from emulsion was studied and compare with emulsion tightness.

3.2. DEMULSIFIER

The demulsifier used in this study were commercially available materials supplied by service companies to oil industry. The chemical composition are not completely known but on the other hand the demulsifiers are known to consist of more than one surface active species. It comprises of a band of ethoxylated propoxylated adducts (mw 2000) together with a cationic fatty acids (mw 800).

3.3 ASPHALTENE SEPARATION:

3.3.1 INTRODUCTION

This method uses the polarity effect to separate hydrocarbons (petroleum) into polar and non-polar fractions by use of excess n-pentane. The maltene fraction (non-polar) is soluble in n-pentane which is non-polar.

3.3.2 APPARATUS AND MATERIALS

Round bottom flask (500 ml), pipettes, Teflon coated magnetic stir bars, Millipore filter (o.5 micron), separatory funnel, Millipore glass filter, test tube, stand, support clamp, electrical magnetic stirrer, and analytical balance, Rotary evaporator and coolant lines.

MATERIALS

n-pentane and methylene chloride.

3.3.3 PROCEDURE

2.00 gram of crude oil was used per 300 ml of pentane.

Separation of Maltene and Asphaltene:

- Wash a glass Millipore filter and a flask with methylene chloride. Dry the flask. Place a 0.5 micron filter onto the Millipore filter and connect the receiving Erlenmeyer flask to vacuum.

- Open the vacuum and start to decant the contents of the round bottom flask through the Millipore glass filter gently. Wash the round bottom flask several times with n-pentane decanting the contents through the Millipore filter after each wash.
- Asphaltene will be collected on the Millipore filter and the matltene which are soluble in n-pentane will pass through the filter and collect in the Erlenmeyer flask.
- Transfer the soluble maltenes from the Erlenmeyer flask to a clean round bottom flask and label it as maltene. Wash the Erlenmeyer flask several times with n-pentane and collect the wash into the maltenes flask after each wash.
- Put the Millipore filter on the Erlenmeyer flask with ethylene chloride to dissolve the asphaltenes. Repeat the washing until all asphaltene are dissolved.
- Put the Millipore filter on the Erlenmeyer flask and connect it to vacuum. Wash the Millipore filter and the round bottom flask with methylene chloride to dissolve the asphaltenes. Repeat the washing until all asphaltenes are dissolved.

- Transfer the asphaltene from the Erlenmeyer flask to the round bottom flask using methylene chloride. Wash the filtration flask several times with methylene chloride and collect the washes in the round bottom flask.

3.4. MALTENE AND ASPHALTENE COLLECTION

3.4.1 MALTENE

- Rotavap the maltene fraction at 50°C to evaporate the n-pentane. The rotavap should be stopped when the maltene fraction reaches about 1 ml in the round bottom flask.
- Transfer the maltenes from the round bottom flask to a test tube using methylene chloride. Wash the flask several times with methylene chloride and collect the washes in the test tube. Put the test tube on the heater at a temperature of about 40°C to evaporate methylene chloride.
- Weigh the test tube and record this weight as maltene gross weight.

3.4.2 ASPHALTENE

- Remove the methylene chloride from the asphaltene fraction by evaporating at 50°C until dryness.
- Transfer the asphaltene fraction from the round bottom flask to the test tube using methylene chloride. Wash the flask several times with methylene chloride and collect the washes into the test tube. Put the test tube on the heater to evaporate methylene chloride.

- Weigh the test tube and record this weight as asphaltene gross weight.

3.5 MOLECULAR WEIGHT DETERMINATION

3.5.1 INTRODUCTION

Vapor Pressure Osmometer is based on the vapor pressure osmometery principle. Small difference in vapor pressure between a pure solvent and a solution are converted to temperature differences which can be measured very precisely with thermistors. When calibrated with a suitable material, the temperature difference can be converted to a molar concentration and thus to molecular weight.

3.5.2 REAGENTS AND MATERIALS

Chemicals used in the determination of molecular weight of wax, resin and asphaltene samples in this study include toluene (HPLC grade).

3.5.3 APPARATUS And PRINCIPAL

Jupitor VPO model 833 was the instrument used in this study for molecular weight determination. It consists of two thermistors which are enclosed in the glass and are pointed up. On the top of thermistors are stainless steel caps that hold a small volume of liquid. The chamber is saturated with solvent vapor at precisely maintained temperature. With

solvent on the top of both thermitors, the bridge that contains these thermistors is balanced (reference zero). The solvent on of the thermistors is then replaced by a solution. Condensation of solvent into the solution from the saturated solvent atmosphere will take place due to lower vapor pressure of the solution. Since solvent condensation release heat, the thermistors that contains solution will be warmed by this process. So, the temperature difference is directly related to the vapor pressure of the solution. The temperature difference between thermistors is measured as a bridge unbalance. Through calibration with a standard material, molecular weights can be calculated from the bridge unbalanced signal. The Schematic is shown in Figure 2

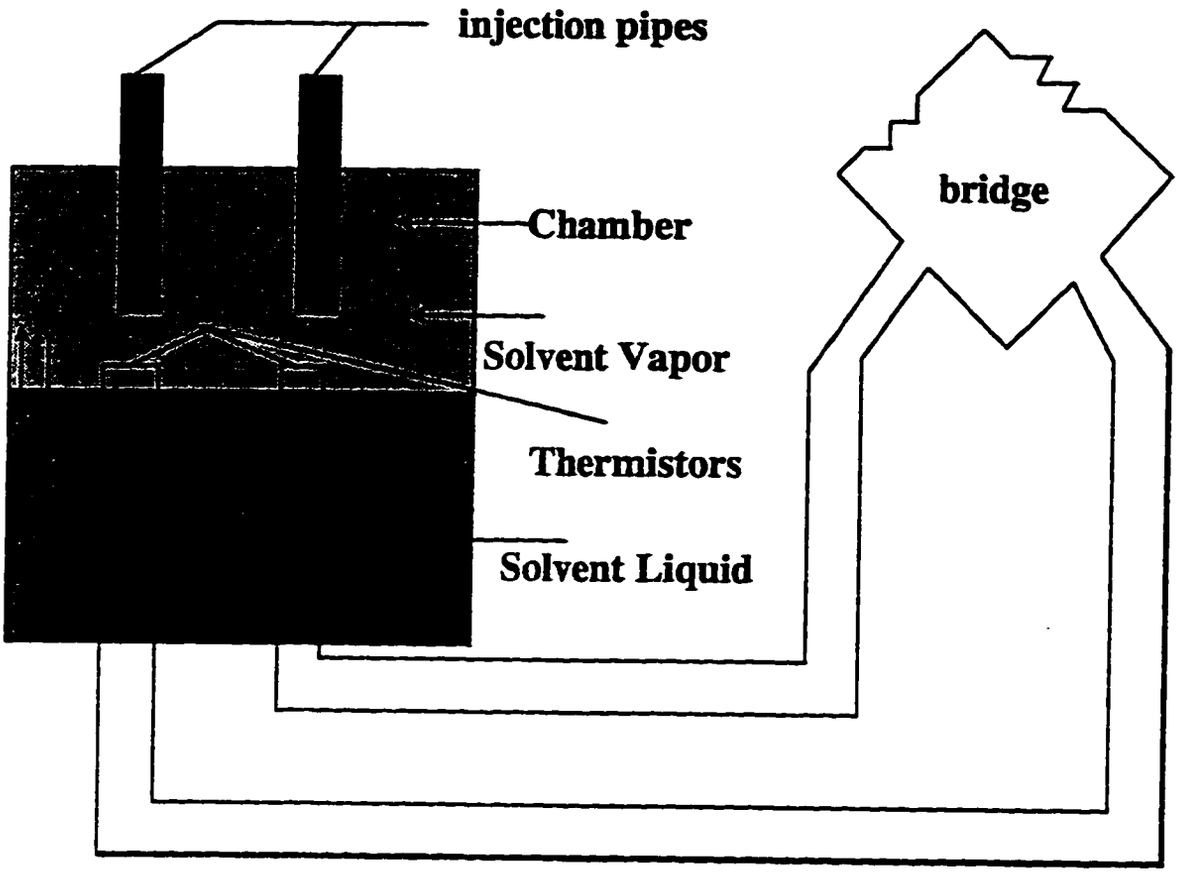


Figure 2. Schematic diagram of vapor pressure osmometer used for determination of molecular weight of asphaltene.

3.5.4 PROCEDURE

The Vapor Pressure Osmometers (VPO) must be calibrated with material of known molecular weight. Standard compounds which have been used successfully in organic solvents include benzil, biphenyl, sucrose octaacetate and squalene. The standard used in this study for the calibration is squalene in toluene. The calibration is started by injecting 20 ml of solvent in solvent reservoir in measuring chamber. Then the instrument is turned on and the cell temperature is set on 50°C which is the recommended operating temperature for toluene. The measuring chamber oven should arrive at the set temperature within 20 minutes, but four hours is recommended to allow the measuring chamber to reach equilibrium. After reaching equilibrium, several solutions of squalene in toluene ranging from(0.7g/l -7g/l) are prepared and a calibration curve is constructed.

With solvent on the top of both thermistors, the bridge that contains these thermistors is balanced. Once the solution was introduced into the chamber and drop of solvent was replaced, solvent condensation from the saturated solvent atmosphere will take place due to lower vapor pressure of the solution. This will cause a difference of temperature between the two drops so, the temperature difference between the thermistors will be measured

and used to calculate the molecular weight. Operating conditions of vapor pressure osmometry measurements are as follows:

The detectable concentration limit : 5×10^{-5}.

The molecular weight determination range : 100-25,000 in toluene.

The cell temperature ranges : ambient to 130°C and will go to sub-ambient with cooling.

The syringe temperature range: ambient to 130°C

The sample volume: 0.25 ml.

The cell ranges : 5, 20, 100 mV

3.5.5 THEORY

Vapor pressure for solvent of sufficiently diluted solution is given by Raoulte's Law:

$P_1 = p_1 x_1$

Where:

P_1 = partial pressure of solvent in solution

p_1 = vapor pressure of pure solvent

x_1 = mole fraction of solvent

by definition $x_1 = 1 - x_2$

where x_2 is mole fraction of solute

so

$P_1=p_1(1-x_2)$ and $P_1-p_1=p_1x_2=dP$

so

$dP= p_1x_2$

For very small temperature change encountered in the vapor pressure osmometer we can assume that T, delta H_v and p are constant. The Clausius-Clapeyron equation written as

$dp/T=pdH_v/RT^2$

after rearranging

$dT = (RT^2/pdH_v)\, dP$

Where:

p = vapor pressure

T = absolute temperature

dH_v = enthalpy of vaporization

R = gas constant

Using the relation $dP = P_1x_2$

$dT = (RT^2/pdH_v)\, P_1\, x_2$

for very small pressure changes $P_1= P$

$dT = (RT^2 / dH_v)x_2$

MOLECULAR WEIGHT CALCUATATION:

By definition

$x_2 = n_2/(n_1 + n_2)$

Where:

n_1 = number of moles of solvent

n_2 = number of moles of solute

For very small n_2

$x_2 = n_2/n_1$

So

$dT = (RT^2 n_2/dH_v n_1) = (RT^2 C_2 m_1/dH_v m_2 1000)$

Where:

C_2 = solute concentration in gram/kilogram

m_2 = solute molecular weight

m_1 = solvent molecular weight

If we denoted all constants in the equation by K_1, then

$dT = (K_1 C_2)/ m_2$

In vapor pressure osmometer, voltage change is proportional to temperature of the thermistors.

$dV = K_2\, dT$

where K_2 contains all instrument constants, so

substituting dT with $(K_1\, C_2)/\, m_2$ we obtained

$dV = K_1 K_2\, dT = K\, C_2/\, m_2$

The calibration factor K is determined for each set of experimental conditions by measuring dV and C_2 for material of known molecular weight (dV/c vs. C) The factor is extrapolated to concentration equal zero. By reversing the procedure, unknown molecular weight can be determined using constant K. The instrument is calibrated with an accurately known molecular weight material. Compound that we used in this study is Squalane (branched aliphatic hydrocarbon with MW. of 422.8). Then the response ,which is change in vapor, is measured vs. concentration of squalane expressed in mole/L.

3.6 SIMULATED DISTILLATION STUDY

3.6.1 INTRODUCTION

Crude oils are generally very complex chemical systems containing from hundreds to thousands of individual components in the range from simple low molecular weight n-alkanes to high molecular weight waxes and asphlatenes. Due to the content of these high molecular weight substances, crude oils are somewhat colloidal in nature [4]. Reservoir crude oils are very

close to thermodynamics equilibrium, but during production, changes of pressure and temperature cause a disturbance of the equilibrium and phase separation like liberation of gas and precipitation of asphaltenes and wax may result [5]. Especially at sub ambient conditions, wax precipitation can deteriorate flow properties and cause sever problems by plugging valves and flow lines. Two types of wax are commonly encountered in crude oils, i.e., macrocrystalline waxes composed of mainly straight-chain paraffins (n-alkanes) with varying chain length (about C20 to C50) and microcrystalline or amorphous waxes also containing a high proportion of isoparaffin and naphthenes (cyclic alkanes) with somewhat higher carbon numbers (C30 to C60); these two types of wax have different properties regarding crystal growth and morphology[7].

3.6.2. PROCEDURE

A calibration curve was constructed by running a known mixture of hydrocarbons covering the boiling range expected in the sample. Using the exact condition and time schedule used in the calibration curve, 0.2-1.0 µl sample was introduced into a gas chromatographic column that separates hydrocarbons in the order of increasing boiling point. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the analysis. Boiling point are assigned

to the time axis from the calibration curve, obtained under the same conditions. From these data, the boiling range distribution can be obtained.

3.7 HIGH PRESSURE GEL PERMEATION CHROMATOGRAPHY (HP-GPC) SEPARATION OF OIL And EMULSION SAMPLES OF ARAB LIGHT CRUDE:

3.7.1 INTRODUCTION

This technique tends to exclude larger molecules from a porous chromatographic stationary phase while small molecules are admitted. As a result, GPC separates primarily on the basis of hydrodynamic molecular size, with the large molecules eluting earlier than small ones. A GPC chromatogram thus provides an estimate of the molecular weight distribution of a sample. From this distribution, number and weight average molecular weights may be estimated. GPC is the only existing analytical method that can routinely-provide information on heavy oil molecular weight distributions.

3.7.2 PROCEDURE

The HP-GPC of asphaltene fraction has been carried out using four μ-styragel columns (10,000, 1000, 500,and 100 A°) and a differential

refractometer. HPLC grade tetrahydrofuran (THF) was used as a solvent mobile phase at ambient temperature (24 ^{0}C) and operating at a flow rate of 1ml/min. The raw data were stored by a Millennium 2010 chromatography manager. The integrity of the system was checked using calibrated polystyrene molecular weight standards. The area under each GPC curve relative to the baseline was assumed to be proportional to the amount of the asphaltene eluted during that time.

3.8 THERMAL ANALYSIS

Differential scanning Calorimetery (DSC) and Thermogravimetric analysis (TGA) are employed to study the compositional analysis of asphaltene, resin and wax material as a function of the temperature.

3.8.1 Differential scanning Calorimetery (DSC)

3.8.1.1 INTRODUCTION

Differential Scanning Calorimetery is a thermal analysis technique which has been used for more than two decades to measure the temperatures

and heat flows associated with transitions in materials as a function of time and temperature. Such a measurements provides quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or change in heat capacity. DSC is the most widely used thermal analysis technique with applicability to polymers and organic materials, as well as various inorganic materials.

DSC has many advantages which contribute to its widespread usage, including fast analysis time (usually less than 30 minutes), easy sample preparation, applicability to both solids and liquids, wide temperature range, and excellent quantitative capability.

In DSC both sample and reference material are subjected to a precisely programmed temperature change. When a thermal transition (a chemical or physical change that result in the emission or absorption of heat) occurs in the sample, thermal energy is added to either the sample or the reference containers in order to maintain both the sample and reference at the same temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. since DSC can measure directly both the temperature and the enthalpy of a transition or the heat of the reaction.

3.8.1.2 INSTRUMENTATION

The instrument used for the thermal analysis of solids, wax, resin and asphaltenes was 910 Differential Scanning Calorimeter, manufactured by Du Pont. The schematic is shown in Figure 3.

3.8.2 THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA provides a quantitative measurement of any weight changes associated with thermally induced transitions. Thermogravimetric curves are characteristics of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges.

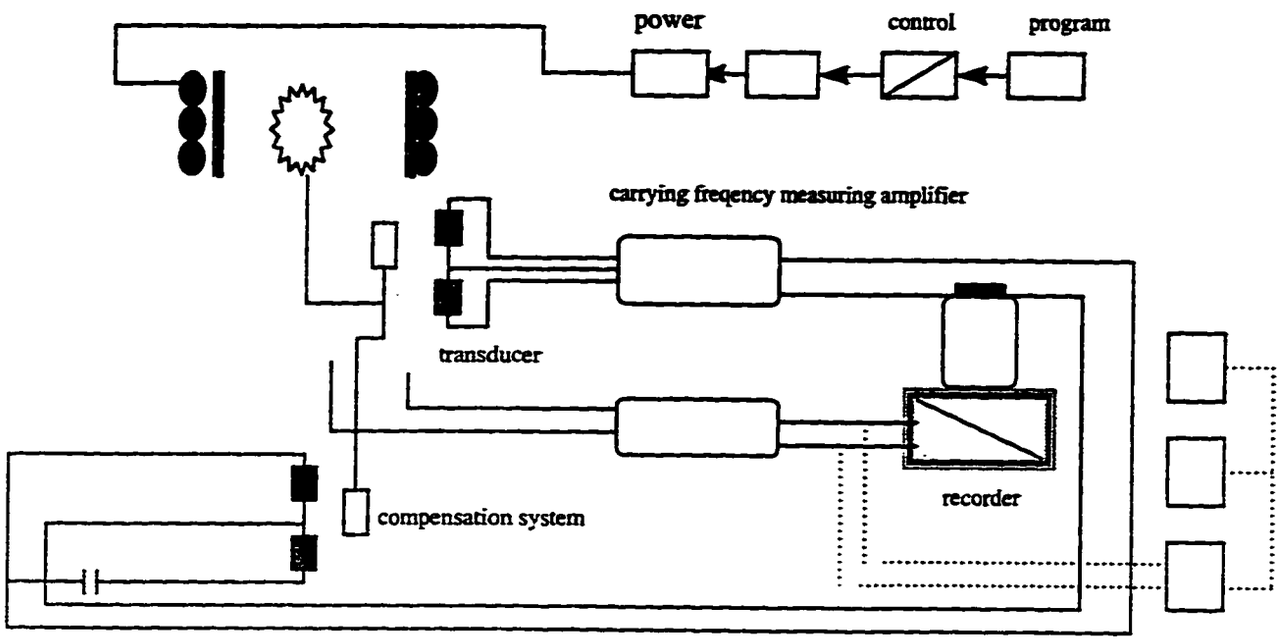


Figure 3. Block diagram for thermogravimetric analysis

3.8.2.1 PROCEDURE

The solids, waxes and asphaltenes separated from emulsion samples were studied using TGA. The sample (40 mg) was grounded to 125 mesh size was placed in alumina crucible. The same weight of aluminum oxide, which undergo no thermal change in the temperature range of the experiment, was placed in an identical alumina crucible as reference sample. By the use of a sample carrier system, which has two sets of thermocouple, the sample was placed in the middle of vertical furnace. The temperature was raised at a uniform rate of 20°C/min. The analyses were made over the temperature range of 25-990°C in a dynamic atmosphere of nitrogen flowing at a rate of 40ml/min. In the thermogram, the weight loss, the differential temperature and the temperature of the sample were plotted simultaneously.

THE CALCULATION OF CHANGE IN ENTHALPY

The change in enthalpy of a sample is equal to the difference between the heat flow to or from the sample, Q_s, and the heat flow to or from the reference material, Q_r:

Change in enthalpy Q_s-Q_r

According to the thermal analog of Ohm's law:

$Q = T_2-T_1/ R_{th}$

The heat flow is directly proportional to difference in temperature and inversely proportional to the thermal resistance, R_{th}.

Combining the preceding relationships yields:

Change in enthalpy = Q_s-Q_r = T_c-T_s/R_{th} - T_c-T_r/R_{th}

Where:

T_c: Constant temperatures external to the sample and the reference

T_s: Sample temperature

T_r: Reference temperature.

The system is designed in such a way to render the two T_c and Two R_{th} identical, so the above equation become:

Change in enthalpy - T_s-T_r/R_{th}

The measured signal is the voltage from the thermocouple or thermopile, which is proportional to temperature difference, (T_s-T_r).

DIRECT MEASUREMENT OF CHANGE IN ENTHALPY

To obtain direct measurement of change in enthalpy, one could integrate the area under a DSC curve according to this equation:

A= -k m dH

Where:

A: is the area

k: is the instrument constant which is temperature independent

H: is the enthalpy of the reaction transition

m: is the mass of the sample.

3.9 INFRA-RED ANALYSIS (IR)

Infrared (IR) spectra of various asphaltene samples were generated using a perkin-Elmer model, producing a spectrum in the wave number range of 4000- 400 cm^{-1}.

The following is the list of samples used for IR characterization:

1) Asphaltenes from well A. This is a well with no emulsion from well head sample.

2) GOSP C production header sample: Oil was separated from GOSP A production header by gravity and oil separated from emulsion by breaking the produced fluid to oil and water completely.

3) Asphaltene samples separated from Well B: These samples are related to oil separated by gravity, and to the oil separated from emulsion by heat and centrifuge.

These FTIR spectra, give very important information on functional groups and their structure features in asphaltene molecules.

All of above samples produced very similar spectra indicating that all of them have similar functional groups.

3.10 SEPARATION OF WAX FROM ARAB LIGHT CRUDE

The wax content of the oils was determined by UOP method 46-85. About 5 g of asphaltene free oil was dissolved in 20 ml of methylene chloride and warmed to 35°C. A methylene chloride cooling bath was maintained at -30°C by addition of dry ice. After 2 h at -30°C, the mixture was filtered through a weighed glass fiber filter, and the filter cake was washed with a cold 30 to 35 ml of cold methylene chloride. The filtrate should be colorless and the wax white. The filter was placed in a tarred bottle and the wax still remaining in the filter funnel was washed into bottle with 20 ml of hexane warmed to 60°C. When the wax is completely dissolved from the filter, the hexane was evaporated at 95°C and the bottle was re weighted to obtain the percentage of total wax in the original sample. The wax was dried in an oven at 105°C for 15 minutes

3.11 COLUMN CHROMOTOGRAPHY

3.11.1 INTRODUCTION

Column chromatography was employed to purify the wax samples by removing the polar fraction (composed of asphaltene and resins)samples from them.

3.11.2 MATERIALS

Solvent utilized were n-hexane, ethylacetate, dichloromethane, methanol and toluene. All solvent used in this study were HPLC grade. Activated silica was used for packing. The silica gel used was 7734-3 SCIENCE, 70-230 mesh ASTM with a size range of 0.063-0.200 mm with iron and chloride contents of 0.03% and 0.02% respectively. The pH of the silica gel used was 7 in 10% aqueous suspension. The column used was 2.5 cm internal diameter and 50 cm height.

3.11.3 PROCEDURE

The column packing materials (silica gel) was activated under vacuum for a period of 48 hours at a temperature of 150°C. Normal hexane (HPLC grade) was used to make slurries. The sample was diluted in small amount of n-hexane to facilitate the transfer of the wax sample to the column.

The wax was eluted through the column using 400 ml of n-hexane with flow rate of 3-4 mls/min. The eluted material was rotovapped under vacuum at a temperature of 40°C to evaporate the solvent.

The resin fraction was eluted using 800 ml of different percentage of ethylacetate in n-hexane. The polarity of the elution solvent was gradually increased by adding successively greater percentage of ethylacetate(20%, 40%,50% , 80%, 100%). This is to make smooth transition from one solvent

to another smooth to avoid cracking the column due to the difference in heat of solvation in binding to adsorbent.

The asphaltene fraction was eluted through the column using 20 % of ethanol in 80% of dichloroethane. The eluted material was rotavapped under vacuum at temperature of 75°C to evaporate the solvent.

3.12 VISCOSITY MEASUREMENTS

3.12.1. INTRODUCTION

The Model 70 viscometer was used to measure the viscosity of both oil and emulsion samples at various temperatures. This viscometer is a coaxial cylinder type was developed to measure fluid reheologies under high pressures and temperatures with a high degree of safety.

3.12.2. INSTRUMENTATION

The FANN design is based on the design of a machine developed by the Sandia National Laboratories. It was designed with oil well and geothermal drilling fluids in mind, but has applications in many fields. Operating Conditions for the Model 70 are as follows:

- Temperatures are limited to 500°F (260°C)
- Pressures are limited to 20000 psig (137900 kpa)
- Sensor system allows for calibration to +/- one degree (one centipoise at 3000 RPM).

- The Viscometer consists from three major components: the Control console, the Remote Test Station, and the Test Cell.
- The Control Console contains all controls and displays, power supplies, the pressurization pump and reservoir, the over pressure relief disk and a removable cell preparation station.
- The Remote Test Station (RTS) is dominated by the vertical, cylindrical safety shield. Viscosity measurements can not be made unless the top of the shield is closed.
- The Test Cell is made of corrosion-resistant metals and is designed for 20000 psig operation at 500°F. It includes a torsion assembly that uses an American Petroleum Institute (API) type bob and rotor geometry.

3.13. POWDER X-RAY DIFFRACTION (XRD) MEASUREMENTS

3.13.1 SAMPLE PREPARATION

Each sample used for x-ray powder diffraction analysis (XRD) was ground to 200 mesh size in a porcelain mortar and pestle. About 1.5 g sample was cemented on top of an aluminum cylinder. The surface of the specimen was pressed, scraped and excess powder was removed to form a flat surface. X-ray powder diffraction patterns were recorded at room temperature using a vertical Q-20 scanning PW-1700 Philips diffractometer.

3.14 PARTICLE SIZE ANALYZER

3.14.1 INTRODUCTION

The Master Sizer X was utilized to measure the size of solids separated form emulsion samples. Low power Helium-Neon laser is used to measure the size structure of solid particle dispersed in a liquid medium. The only qualification of the technique is that each phase must be distinct optically from the other and the medium must be transparent to laser wavelength.

3.14.2 APPARATUS

The apparatus use to measure the size particle is composed of a laser source, spatial filter, spray nozzle, fourier tansform lens, detector, and obscuration monitor.

CHAPTER 4

RESULTS AND DISCUSSION:

4.1. SOURCE OF THE SAMPLES

The emulsion samples were obtained from problem and non-problem GOSPs, where over 40 wells flow to each GOSP. Also, three problem wells (B,C,D), and one non-problem well (A) were studied. Samples were obtained upstream of chemical injection facilities and are, therefore, considered demulsifier-free. Therefore these three GOSPs and Four wells were selected for our investigations.

4.2. PRODUCTION HEADER SAMPLES FROM VARIOUS GOSPS

Solids present in produced fluids from GOSP A, GOSP B and GOSP C are separated by successive toluene dilution and centrifugation. The results of these tests are shown in Table I. These data indicate that the separated solid samples are increasing in the following order:

GOSP C > GOSP B > GOSP A. Samples collected from GOSP A under pressurized condition contains only 13 mg/l of solids where as for GOSP B this is 60 mg/l and for GOSP C it is 165 mg/l. In addition to these, the other data in Table I indicate that samples collected from these GOSPs under the

flashed condition contain significantly more solids than those samples collected under pressurized conditions. This may be due to the formation of additional $CaCO_3$ (calcite) due to release of CO_2 gas at high temperatures as samples are collected under atmospheric condition. At these temperature,(over 150 °F), the solubility of CO_2 is low, and once the hot fluid is collected at atmospheric pressure, the CO_2 gas is released, that affects the thermodynamic equilibrium of Carbonate system where $CaCO_3$ can be formed as shown in Figure 4.

TABLE I

SOLIDS SEPARATED FROM VARIOUS PRODUCED FLUIDS AT DIFFERENT GOSPS

GOSPS NO.	SAMPLE TYPE	% BY WEIGHT	mg/l
A	Flashed	0.0066	56
A	Pressurized	0.0015	13
B	Flashed	0.0255	195
B	Pressurized	0.007	60
C	Flashed	0.0285	279
C	Pressurized	0.019	165

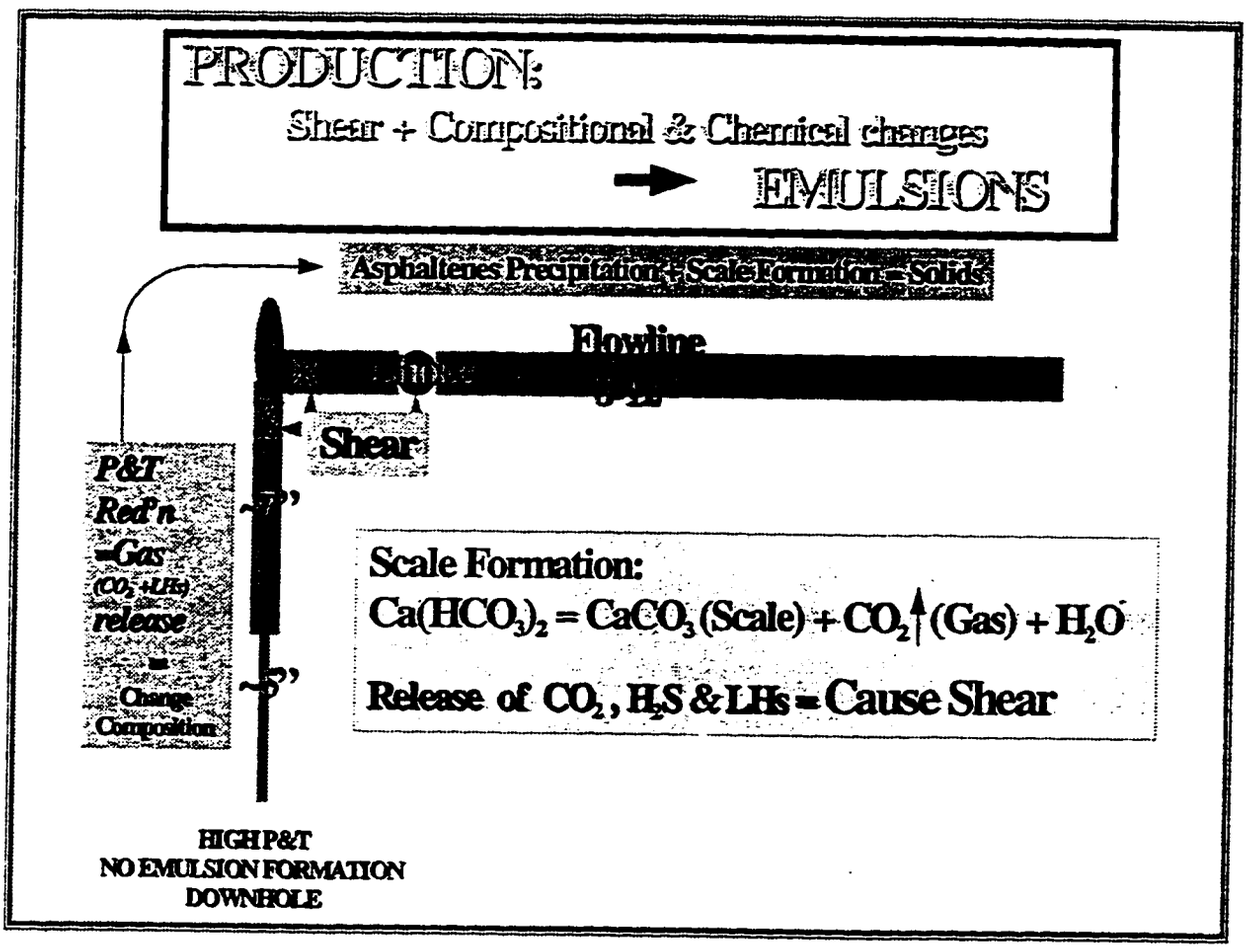


Figure 4. Effect of pressure and temperature on solids formation

4.3 COMPOSITION OF EMULSION STABILIZING SOLIDS BY TGA And DSC

Tests are conducted on solid samples separated from GOSPs A,B and C production header emulsion (which is collected under pressurized condition). The results are shown in Figures 5, 6, and 7.

Figure 5 shows the Thermogravimetric analysis (TGA) diagram of the solids under the air for GOSP A. As it is clear from this diagram that at the temperature of above 200°C a major weight loss starts to occur, and at 330°C over 25 % of the sample is lost. This can be attributed to wax and other volatile material present in the samples.

As the temperature of the sample is increased from 330°C to 380°C no significant weight loss was observed, at that temperatures. At about 450°C a major weight loss is again occurred and over 30% of sample was lost at these temperatures. This is the area where most of the polar material such as asphaltenes and resins are cracked and combusted. Almost all of the organic matter is combusted below the temperature of 650°C. Above these temperatures inorganic matters could start decomposing. This is about 45% of the total weight of the sample.

Figure 6 shows a TGA test conducted under air for GOSP B. This indicate similar behavior and the weight loss in this test is due to the release of volatile and combustion of polar heavy organic matters at high temperatures. At the end of the test, residual carbon as well as inorganic matter which is not decomposed remained. This is about 25% by weight.

Figure 7 shows the Thermogravimetric analysis (TGA) diagram of the solids under the air for GOSP C. As it is clear from this diagram that at the temperature of above 200°C a major weight loss starts to occur, and at 330°C over 50 % of the sample is lost. This can be attributed to wax and other volatile material present in the samples.

As the temperature of the sample is increased from 330°C to 380°C no significant weight loss was observed, at that temperatures. At about 450°C a major weight loss is again occurred and over 35% of sample was lost at these temperatures. This is the area where most of the polar material such as asphaltenes and resins cracked and combusted. Almost all of the organic matter are combusted below the temperature of 650 °C. Above these temperatures inorganic matters could start decomposing. This is about 15% of the total weight of the sample.

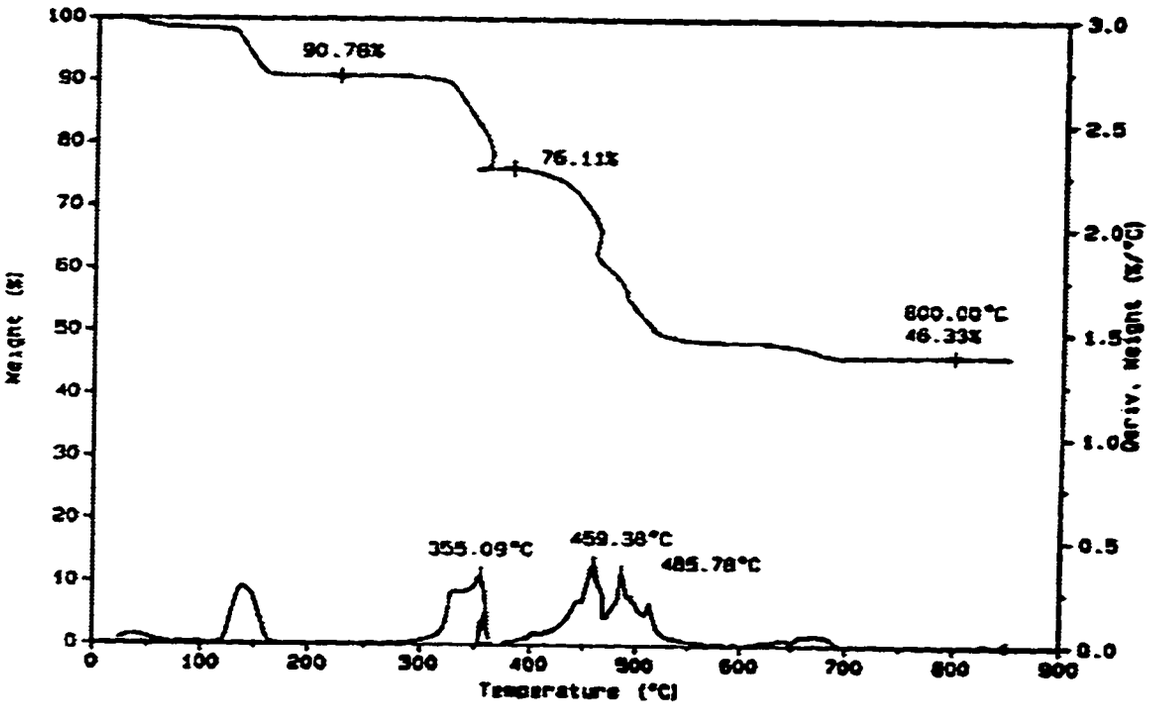


Figure 5. TGA PLOT: for solids separated from GOSP A

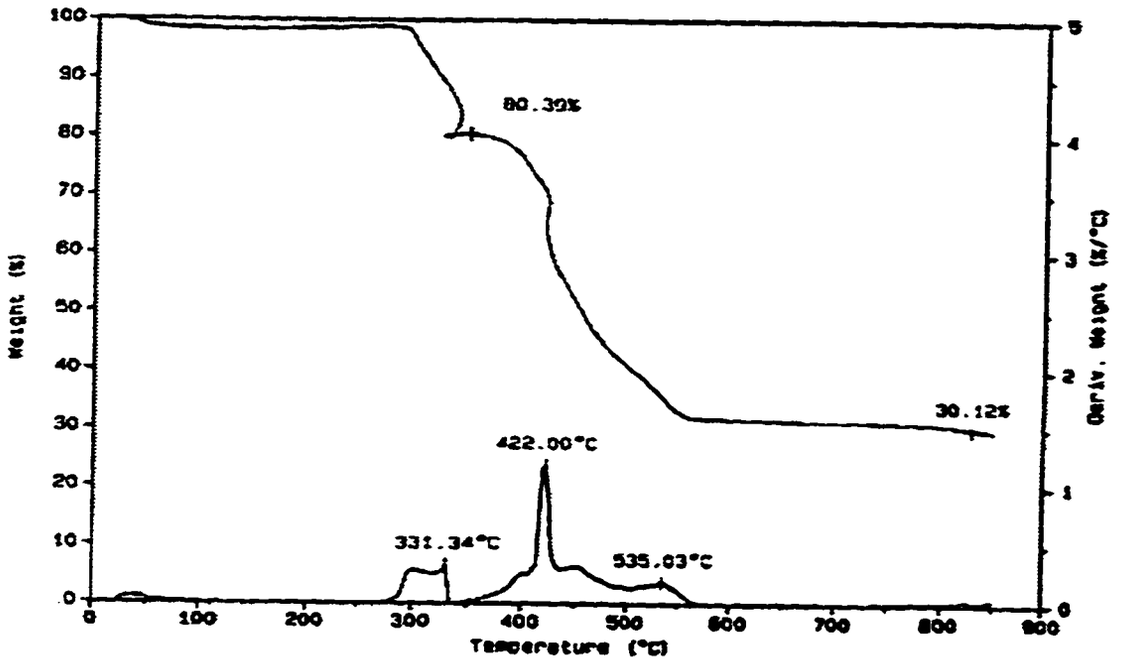


Figure 6. TGA PLOT: for solids separated from GOSP B emulsion sample.

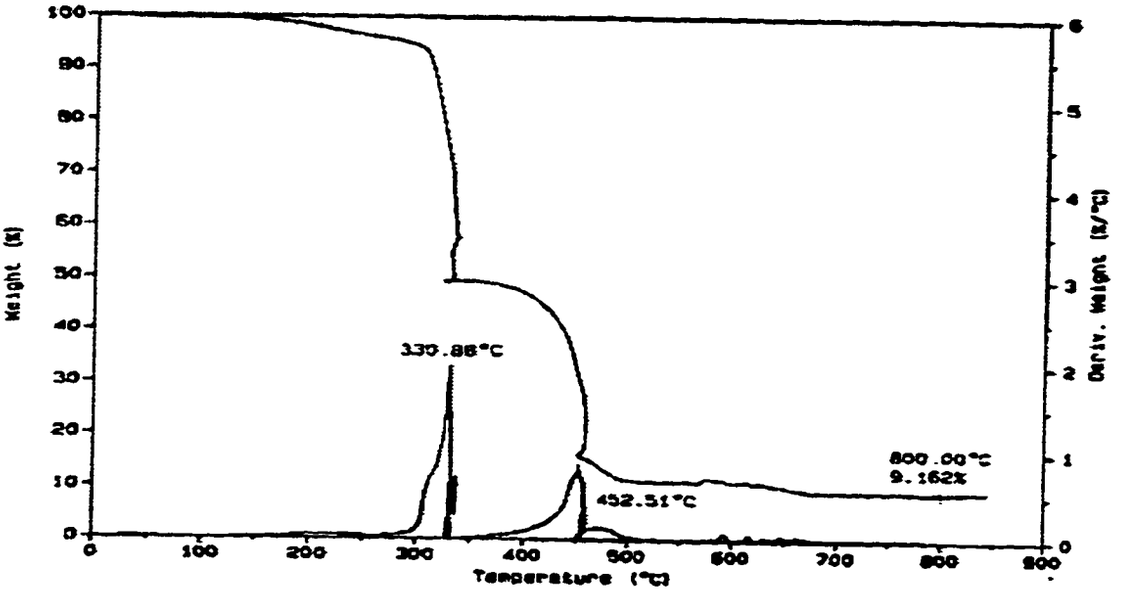


Figure 7. TGA PLOT: for solids separated from GOSP C emulsion sample.

In Figures 8,9&10 the DSC tests for solids from GOSP A,B and C. This shows a peak for heat flow at 90-100 °C. This is related to the melting of the sample at these temperature confirming that the solid sample contains wax material. Peak for GOSP C is much sharper than other two GOSPs indicating a larger quantity of waxes. Therefore based on these tests and XRD data, which will be discussed latter, one can roughly estimate the composition of each solids (caused the emulsion problem).

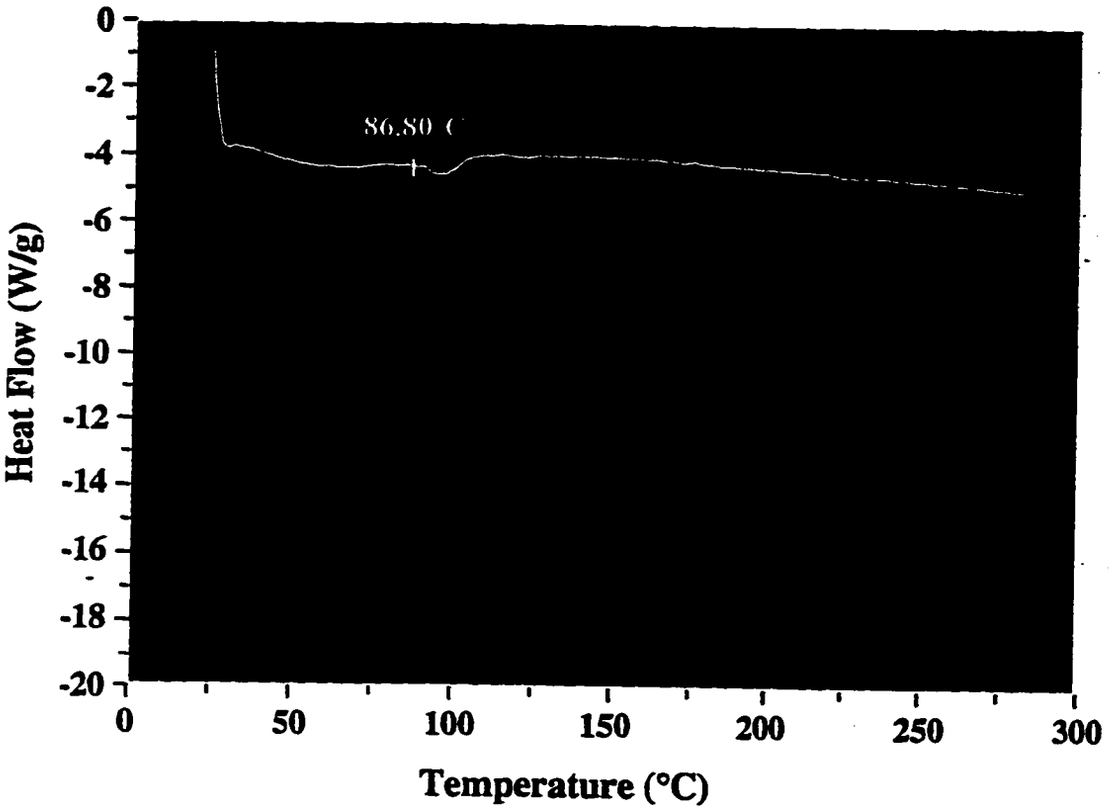


Figure 8. DSC PLOT: For solids separated from GOSP-A emulsion sample

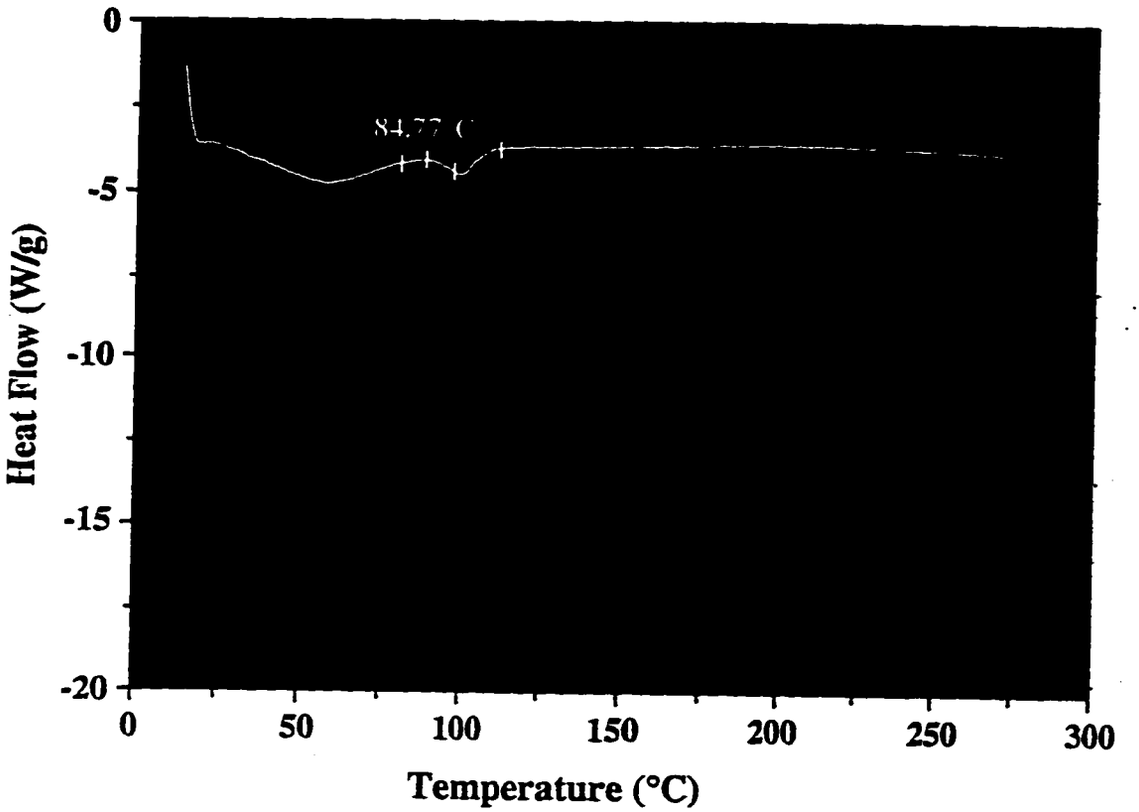


Figure 9. DSC PLOT: For solids separated from GOSP-B emulsion sample

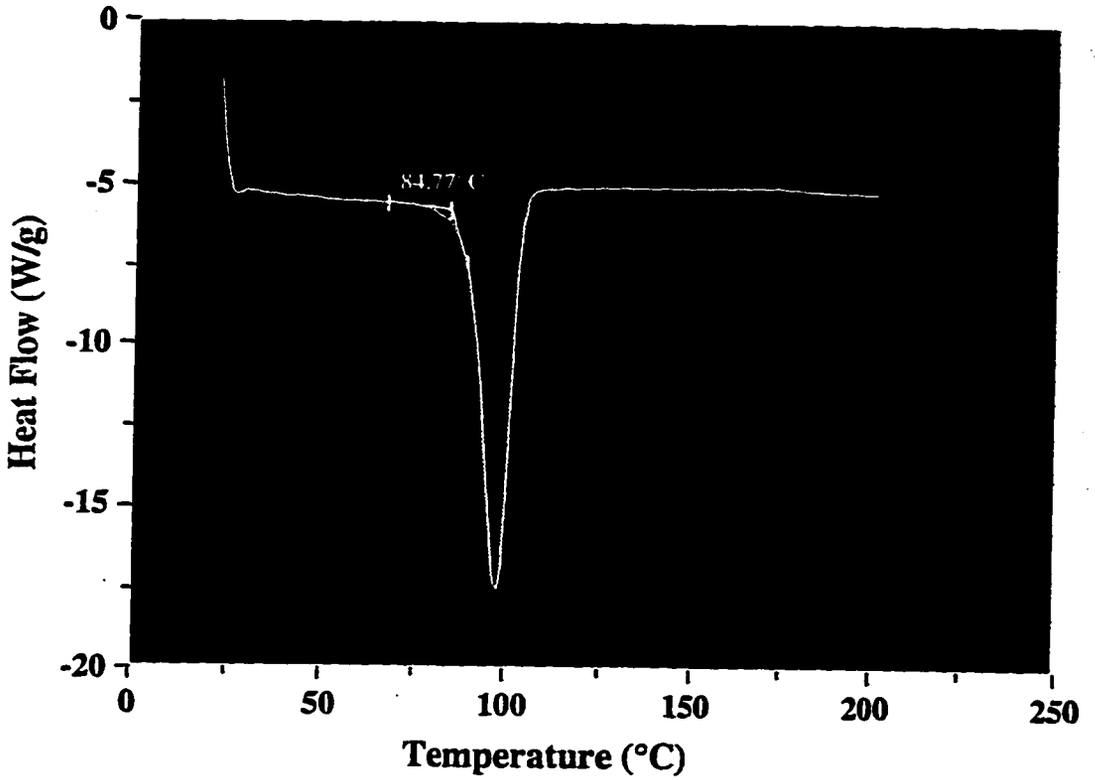


Figure 10. DSC PLOT: For solids separated from GOSP-C emulsion sample

4.4. VISCOSITY MEASUREMENTS

The viscosity data are reported for all of the samples collected from three GOSPs (A, B, C). These are reported in Table II. It is evident from the data that flashed samples have a higher viscosity than samples collected under pressurized conditions. It reveals that the fluid collected under flashed conditions forms tighter emulsions. This is due to the formation of additional calcite as a result of flashed sampling which stabilized emulsions as well as the additional shearing which is introduced into the sample during the sampling process.

4.5. PRODUCTION HEADER SAMPLES FROM VARIOUS WELLS

Well head produced fluid samples are collected from well A,B,C and D under the pressurized conditions. Then the solids were separated from these samples. The data is shown in Table III. It is clear from this table that well A, which is non-problem well, produced fluid gave 20 mg/l of solids where as the produced fluid of well B, which is problem well gave 540 mg/l of solids. The other two wells, well C and D gave 177 and 118 mg/l respectively.

TABLE II

VISCOSITY MEASUREMENT FOR VARIOUS PRODUCED FLUIDS COLLECTED FROM DIFFERENT GOSPS

GOSP NO	SAMPLE TYPE	VISCOSITY (cp.)			
		21°C	43°C	66°C	88°C
A	Flashed	18	13	9	5
A	Pressurized	14	11	7	4
B	Flashed	18	13	9	5
B	Pressurized	13	11	7	4
C	Flashed	19	13	9	5
C	Pressurized	16	11	7	4

TABLE III

SOLIDS SEPARATED FROM VARIOUS WELLS

Wells	Solids (mg/L)
Well A	20
Well B	540
Well C	177
Well D	118

4.6. EFFECT OF WELL HEAD CHOKE SETTING ON VISCOSITY OF PRODUCED FLUID

The effect of chokes, to restrict wells for reservoir control, has been observed to exacerbate emulsion formation, as evidenced by increased demulsifier consumption in the Saudi Aramco's GOSPs. The study of this phenomenon was selected to enable us to identify and determine the data required for emulsion tightness classification and evaluate techniques for the handling of the results obtained.

Pressure samples were collected from four GOSP C at the following three different choke settings:

- Fully open (172/64"): - two samples collected, Upstream of the choke (as baseline) and downstream,
- Half open (80/64"): - sampled downstream;
- Quarter open. (36/64"): - sampled downstream.

A sample was also collected from the GOSP production header (upstream of demulsifier injection) for comparison. Viscosity of produced fluid from Well-B at different temperatures (43, 66, 88°C) is shown in Table IV. The data indicate that increased choke setting causes an increase on emulsion stability.

TABLE IV

EFFECT OF CHOKE SETTING ON VISCOSITY OF PRODUCED FLUID FROM WELL-B

CHOKE SETTING	SAMPLE TYPE	VISCOSITY (CP)		
		110°F	150°F	190°F
FULL OPEN (174/64)	FLASHED	14	9	6
	PRESSURIZED	12	8	5
HALF OPEN (80/64)	FLASHED	15	9	7
	PRESSURIZED	14	8	7
1/4 OPEN (36/64)	FLASHED	16	10	7
	PRESSURIZED	15	9	7

4.7. COMPOSITION OF EMULSION STABILIZING SOLIDS BY XRD

The results of XRD data were summarized in Table V. XRD techniques will only give a good information on crystalline matter present in various emulsion samples. Asphaltene and any other solid matters which are not in a crystalline form can not be quantified by this method. Results shown in Table V indicate that the crystalline matter present in these samples are paraffin, calcite and aragonite. Solids from the GOSP-A pressurized sample contain paraffin crystals, calcite and small percentage of geotite . No aragonite, which is another form of crystal of calcite, matter was found in solids separated from GOSP-B and GOSP-C pressurized fluid samples. These samples also contained higher percentage of paraffin and calcite crystalline particles. However, our visual observation indicated that all of these samples contained asphaltene matter in addition to paraffin and calcite which are detected by XRD. As asphaltene particles can not be analyzed by XRD therefore based on the XRD data we can not quantify the exact amount of each of these components (wax, asphaltene and calcite) which are responsible for emulsion formation. In addition, comparison of XRD composition of flashed samples with those of pressurized samples indicates that flashed samples contain a higher weight % of calcite particles. This confirms the

above mentioned hypothesis that, as CO_2 gas is released during collection of the flashed samples, additional Calcite particles are formed which are contributing to the tightness of these emulsion samples. Therefore samples must be collected at pressurized conditions for any investigation to get a realistic understanding of emulsion properties and to avoid formation of a significant amount of $CaCO_3$ which can affect the emulsion properties especially its tightness.

TABLE V

X-RAY DIFFRACTION FOR CRYSTALLINE COMPOUNDS

GOSPs	PARAFFIN %	CALCITE %	AROGNITE %	GEOTITE %
GOSP A	25	74	0	1
GOSP B	40	59	0	1
GOSP C	75	23	1	1

SUMMARY OF COMPOSITION RESULTS

The solids content of the various GOSPs emulsions determined by XRD&TGA methods are in Table VI. The total quantity of the solids (Paraffin, Asphaltene/resin ratio, and Calcite) are all increasing in the following order:

GOSP C> B>A. This correlates with emulsion tightness as the emulsion tightness is also in the same order. Thus it can be concluded that all of the solids are contributing to the emulsion stability.

TABLE VI

COMPOSITION OF SOLIDS FROM VARIOUS GOSPS
BASED ON XRD & TGA

GOSP	PARAFFIN (PPM)	ASPHALTEN + RESIN (PPM)	CALCITE + OTHER INORGANIC (PPM)	TOTAL (PPM)
GOSP A	2	5	6	13
GOSP B	13	33	14	60
GOSP C	86	59	20	165

4.8. MICROSCOPIC ANALYSIS OF EMULSIONS:

Samples of tight and semi-tight emulsions are collected from two different points at the field and are examined under a light microscope. It was observed that all of the emulsion samples were water-in-oil type. Also, the presence of dark film containing dark solids was observed at the oil water interface (around the water droplets) in all of the emulsion samples. Addition of xylene removed most of these interface materials, indicating that they were mostly organic materials with some inorganic solids (insoluble in xylene).

Photomicrographs from emulsions are shown in Figures 11&12 respectively.

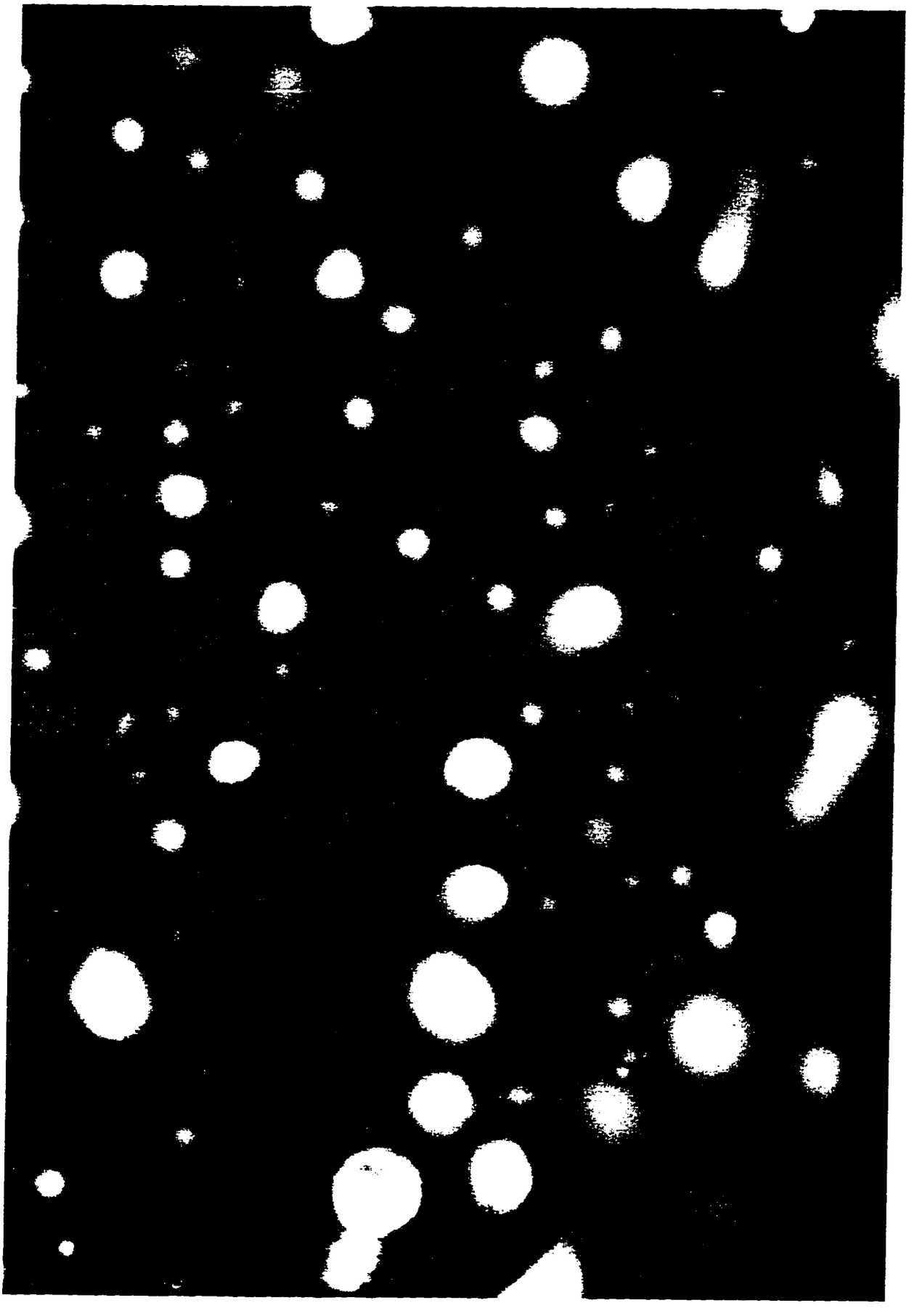


Figure 11: Photomicrograph of an emulsion sample.

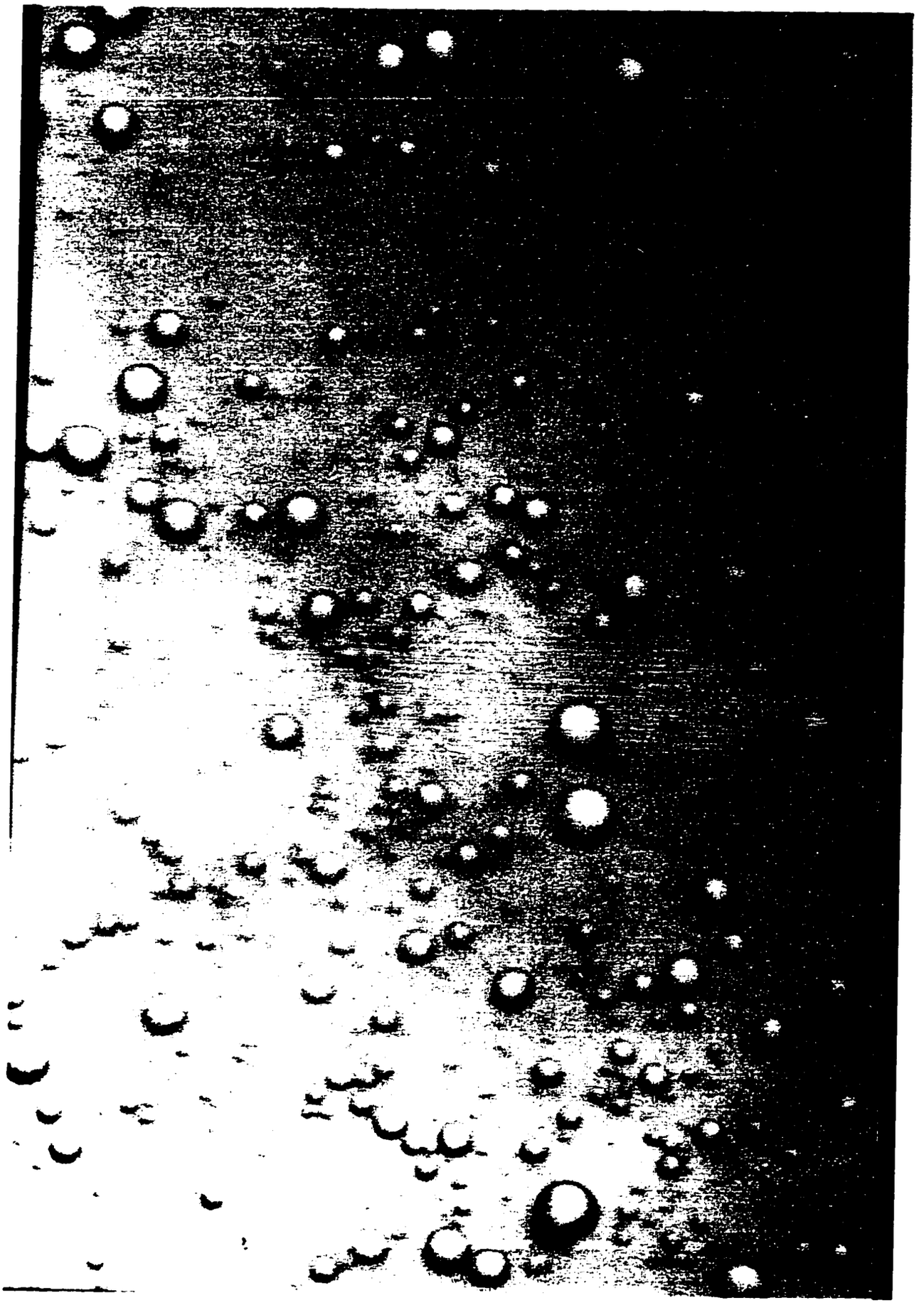


Figure 12: Photomicrograph of emulsion sample with xylene addition.

4.8.1. SEMI-TIGHT EMULSION:

Figure 13 shows the plot of percentage of droplets as well as cumulative percentage of droplets vs. droplet size for an emulsion sample collected at the production header up stream (u/s) of demulsifier injection. The data indicate that the droplet size of water varied between < 5 and over 200 microns, 10% of the droplets were over 80 microns. The median droplet size for this emulsion sample was about 21 microns, and the highest population of droplets were in the range of 15 to 20 microns.

4.8.2. Tight Emulsion:

Figure 14 shows the droplet size distribution for an emulsion sample obtained from tight emulsion. Comparison of data shown in this figure with those shown in Figure 13 indicate that the population of larger droplets were further reduced, and the median droplet size was reduced significantly from 20 microns to 15 microns. This indicates that demulsifier had more time to react and coalesce the water droplets and that the relative population of smaller droplets was increased. In Table VII all of the above data is summarized.

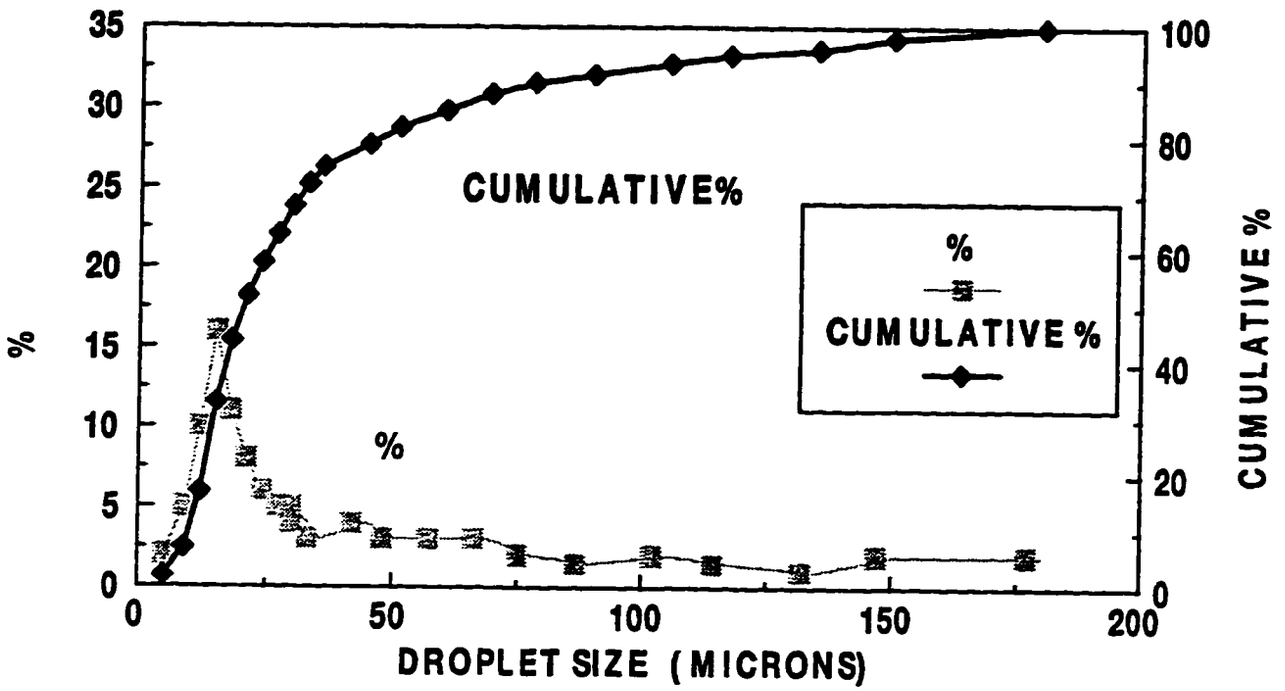


Figure 13. droplet size distribution for semi-tight emulsion sample.

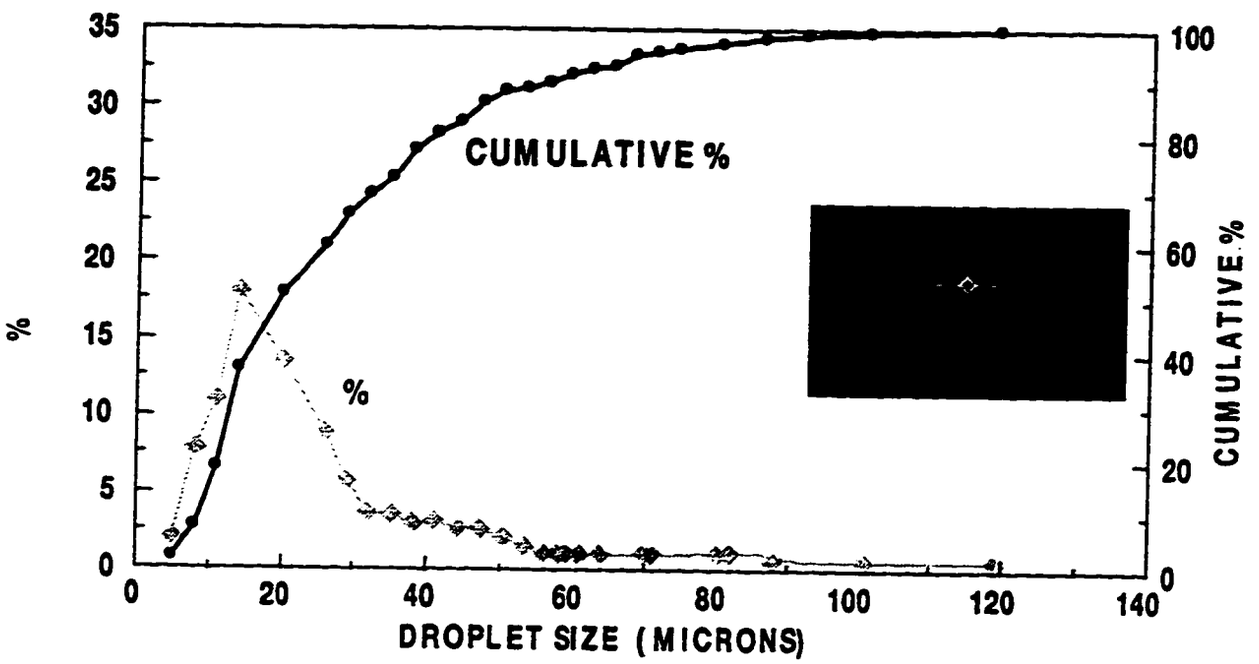


Figure 14. droplet size distribution **for tight emulsion sample**

4.8.3. Effect Of Xylene Addition:

A drop of xylene was added to a fresh emulsion drop on the microscope slide during the microscopic examinations to see its effect on emulsion. It was observed that xylene dissolved most of the dark brown interface film. As most of dark brown material was dissolved and diluted in the xylene, it become easier to observe the droplets as the amount of transmitted light was increased. This was, due to the fact that water droplets were stabilized by organic and inorganic material (which is coated with organic material)and the addition of xylene dissolved the organic coated materials. As a results, dispersed droplets become unstable and immediately larger water droplets coalesced after the addition of xylene. Figure 15 shows the droplet size distribution of the emulsion sample immediately after the addition of xylene. Comparison of Figure 15. with Figure 13 indicates that droplet size range was reduced significantly (> 5- 50 microns). This indicates that all of the water droplets with over 50 microns were completely coalesced. The median droplet size was also reduced from 20 to 17 microns. Additional information is given in Table VIII. This experiment indicates that even though the addition of xylene helps to examine the droplet under the microscope, however it will effect the droplet size distribution analysis. Therefore droplet size data will not be fully correspondent to the original emulsion sample.

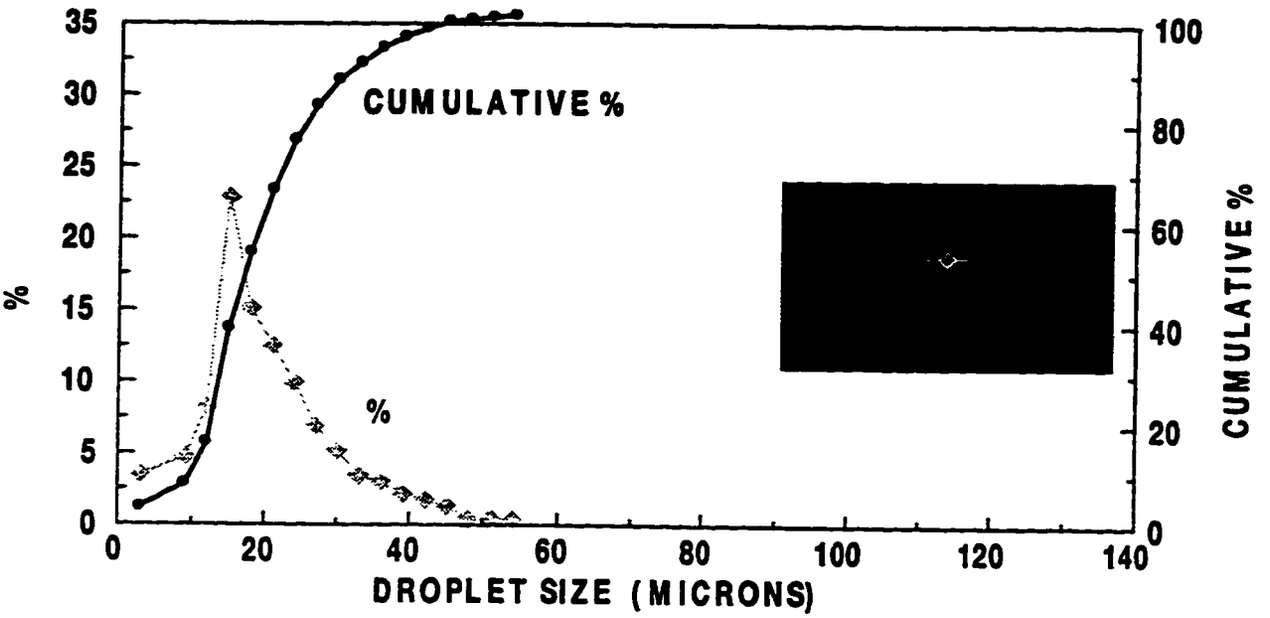


Figure 15. droplet size distribution for semi-tight emulsion sample after xylene addition.

TABLE VII

DROPLET SIZE DISTRIBUTION FOR VARIOUS EMULSIONS SAMPLES

	Droplet Size Range (Microns)	Median Droplet Size(Microns)	% Droplet Under 15 Microns	% Droplet Under 80 Microns
Semi-tight emulsion	> 5 - < 200	21	30 - 35	90
Tight Emulsion	> 5 - 120	15	50 - 55	98

TABLE VIII

EFFECT OF XYLENE ON DROPLET SIZE DISTRIBUTION DURING MICROSCOPIC EXAMINATION

	Droplet Size Range (Microns)	Median Droplet Size (Microns)	% Droplet Under 15 Microns	% Droplet Over 50 Microns
Sample Before Xylene Addition	> 5 - 120	20	35 - 40	10
Sample After Xylene Addition	> 5 - 50	17	40 - 45	0

The following observations may be summarized for above study:

- Tighter emulsions have smaller droplet size than looser emulsions.
- Addition of xylene removed some of the dark colored solid material present at droplet oil-water interfaces. However, some of the solid material, being insoluble in xylene, remained at the interfaces. This indicates that both organic and inorganic particles are present at the interface.
- Addition of demulsifiers breaks oil in water emulsion. However, oil-in-water and oil-in-water-in-oil emulsions were still observed after demulsiifer addition.

4.9. ORGANIC SOLIDS

4.9.1. Asphaltene, Resin interaction and A/R ratios:

Resins increase the solubility of asphaltene in the crude, minimizing the asphaltene interaction with water droplets. The Resin/Asphaltene ratio (R/A) may therefore be expected to provide valuable information on tight emulsion formation. The following tests were conducted to test this hypothesis.

a) R/A ratio was determined for oil collected from a non problem well.

b) R/A ratio was also determined for fractions of an oil sample, separated by increasingly rigorous demulsification steps, from a problem well.

Results (obtained using SARA analysis) are in Table IX.

A comparison of the R/A ratio obtained for non problem wells with those of problem wells indicate that, in general, oil fractions which are separated easily have higher R/A ratios than those separated from tight emulsions using centrifugation or addition of demulsifiers. This indicates that R/A decreases as emulsions become tighter and harder to break. This again confirms that asphaltenes play a key role in stabilization of emulsions. A higher concentration of resins keeps more of the asphaltene aggregate dissolved in the oil phase. This, therefore minimizes the amount of asphaltene aggregate which is able to move to the oil water interface, contributing to the stability of interface film and to tight emulsion formation.

TABLE IX

COMPARISON OF RESIN/ASPHALTENE RATIOS FOR OIL PHASES SEPARATED FROM TIGHT EMULSION PRODUCING WELL, WITH OIL FROM NON PROBLEM WELL.

PROBLEM WELL-C

Sample type from problem well	R/A Ratio
Free oil separated by Gravity	3.8
Oil separated by Centrifuge @ 120^{O}F	3.5
Oil separated by Centrifuge @ 160^{O}F	3.1
Oil separated from the remaining emulsion by Demulsifier and Heat	2.6

NON-PROBLEM WELL-A

Sample type from non-problem well	R/A Ratio
Free Oil separated by Gravity	4.6

TABLE X

COMPOSATIONAL DATA OF CRUDE OIL OBTAINED FROM PROBLEM WELL

Sample Type	Saturates Wt%	Aromatics Wt%	Resins Wt%	Asphaltenes Wt%	S/A Ratio
Top Oil Separated By Gravity	45.1	44.4	8.1	2.4	3.4
Oil Separated By 1st Stage Centrifuge (@130° F)	45.0	44.6	7.2	3.2	2.3
Oil Separated By 2nd Stage Centrifuge (@160° F)	36.5	44.0	13.4	6.1	2.2
Oil Separated By 2nd Stage Centrifuge (With Demulsifier@160° F)	40.0	43.5	9.5	7.0	1.4

4.10. ASPHALTENE CHARACTERIZATION:

We have identified that stable emulsions have lower R/A ratios than unstable emulsions. In this study, various asphaltenes samples separated from emulsions were examined as follows:

Three different oil fractions are separated from produced fluid from well C. These fractions are prepared based on their ease of separation from the produced emulsions as follows:

1) Oil separated by gravity from the well head sample.

2) Oil separated by heat and centrifuge from the emulsion layer after removing oil separated by gravity (after step 1 of the well head sample).

3) Oil separated by heat, centrifuge and demulsifier addition from the remaining emulsion layer after removing some oil by heat and centrifuge (step 2) of the well head sample.

The asphaltene separated from these sample was analyzed by FT-IR to see if there is any significant difference among various asphaltenes separated from these different emulsions with different tightness.

4.10.1. FOURIER TRANSFORM INFRARED SPECTROSCOPY OF ASPHALTENES

1) Figures 16 and 17 show IR spectra asphaltene samples separated from oil samples of produced fluid collected from well C described above in step 1 to step 3.

2) GOSP C production header sample: Figures 18 and 19 show IR spectra of asphaltene separated from oil resulted from breaking the produced emulsion fluid collected from GOSP C production header.

3) Figure 20 shows IR spectrum asphaltene separated from oil collected from well-A. This is a well with no emulsion problem..

All of above samples produced very similar spectra indicating that all of them have similar functional groups.

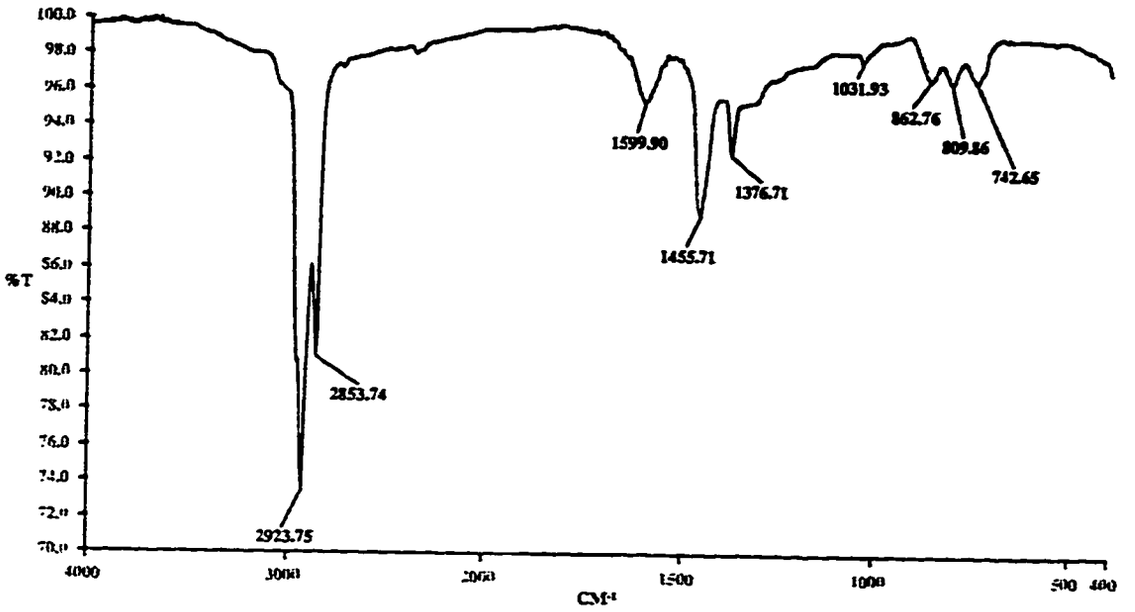


Figure 16. FTIR spectrum: asphlatene sample separated from a well B oil sample .

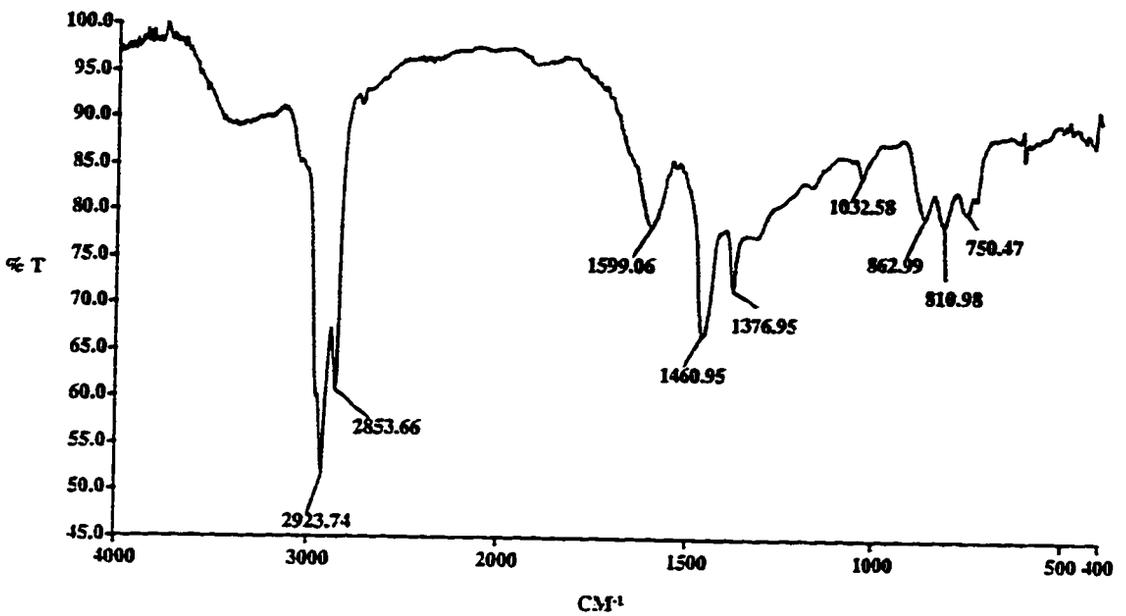


Figure 17. FTIR spectrum: asphaltene sample separated from a well B emulsion sample

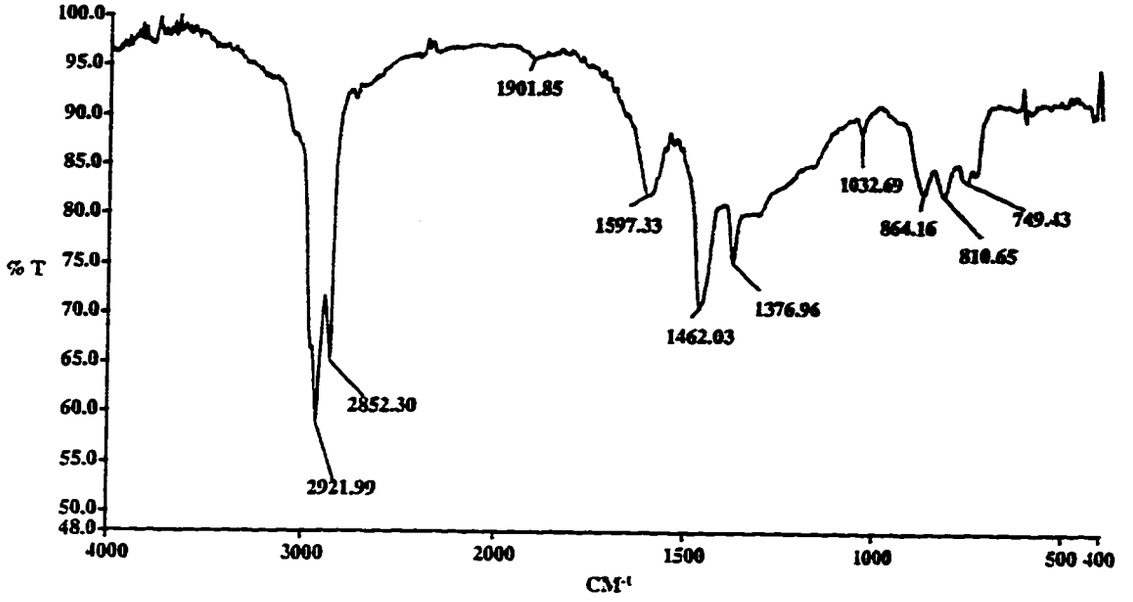


Figure 18. FTIR spectrum: asphlatene sample separated from a GOSP C free oil sample.

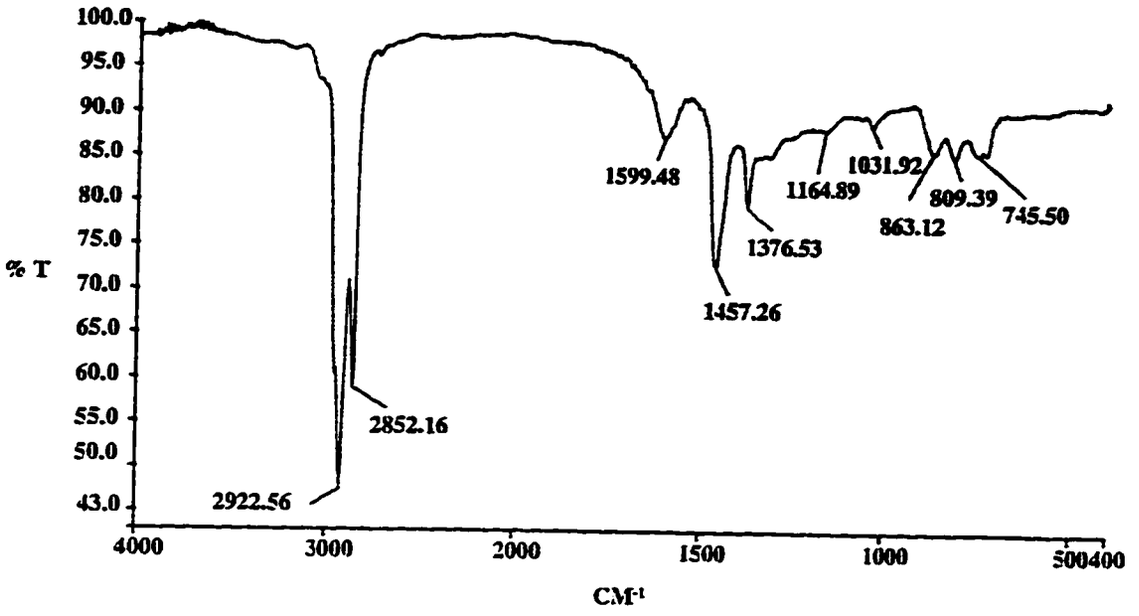


Figure 19. FTIR spectrum: asphlatene sample separated from a GOSP C emulsion sample.

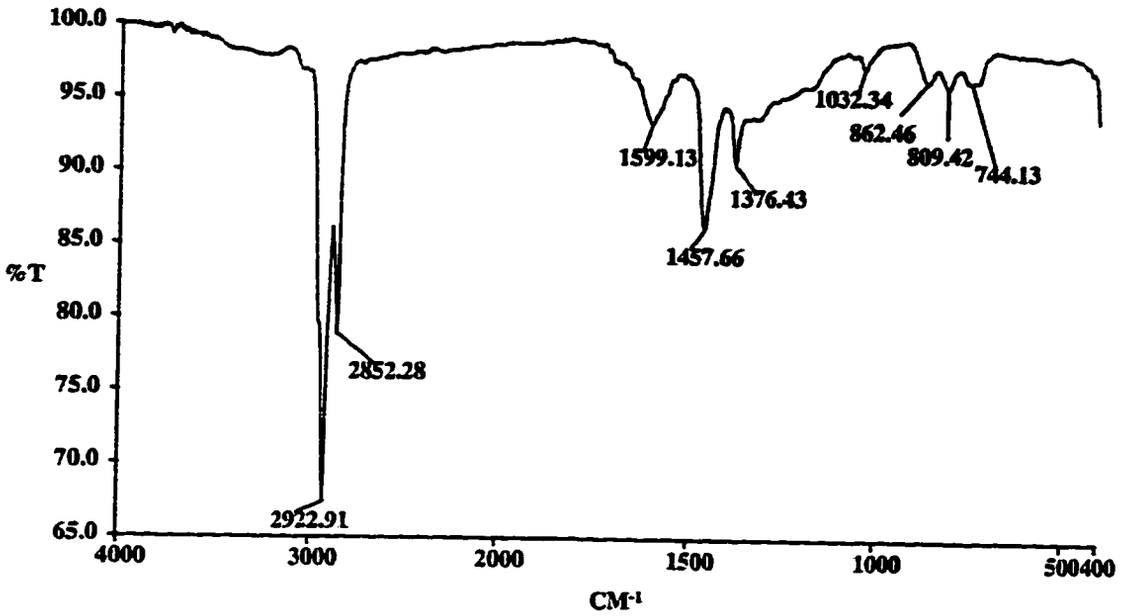


Figure 20. FTIR spectrum: asphaltene sample separated from a well a free oil sample

The following is a brief description of these spectra:

- The region of 3500-3100 cm^{-1} relates to aliphatic hydrogen bonded group such as free OH (at 3610 cm^{-1}) and free N-H (at 3480 cm^{-1}). Very weak absorption peaks were observed in this region indicating the absence of these functional group.
- The spectra of all samples show two distinct absorption peaks at 2920 cm-1 and 2852 cm^{-1} and a shoulder at 2970 cm^{-1}. These are characteristic of C-H symmetric and asymmetric vibrations.
- A very weak signal at 2720 cm^{-1} relates to the dimers of carboxylic acid present.
- Various weak peaks in the region of 2000- 1800 cm^{-1} are present, these are indicative of overtone bands of highly aromatic polycondensed compounds with long-chain substituents
- Peak at 1597-1600 cm^{-1} relates to C=C (double bonds) for aromatic systems. Also oxygen- containing groups indicating this peak.
- A peak at 1376- 1377 cm^{-1} relates to C-H symmetrical bending vibrating of methyl groups.
- The small peak at 1032-1033 cm^{-1} is indicative C-O stretching in aliphatic structure which indicates the presence of ether linkage.

- various peaks at low frequencies of 864,812,750 and 742 relates to H-C-C rocking vibrations. This peaks will confirm the presence of aromatic system.

4.11. EFFECT OF TEMPERATURE AND PRESSURE ON ASPHALTENE FLOCCULATION

Changes of temperature and pressure both play a critical role in asphaltene precipitation and hence on emulsion formation, decrease of pressure above the bubble point will reduce asphaltene solubility. However below the bubble point, the change in the oil composition induced by gas liberation will enhance asphaltene solubility upon pressure decrease. Temperature dependence of asphaltene solubility is an even more complex matter, as various phenomena take place during the temperature change (Figure 21). As an example, thermal expansion of the crude, and reduction of asphaltene/resin interaction oppose the increase of solubility caused by increasing the temperature.

During the production of oil a significant decrease in the Pressure & Temperature of the produced fluids takes place. The pressure decreases from that of reservoir to about 50 PSI. Temperature decreases from about 220°F to 70-140°F, depending on the ambient temperature. As these changes occur, asphaltene particles can be separated. These particles will not easily

dissolve back into the oil phase. They remain suspended at the oil water interface, contributing to the stability of the oil water interface film and so enhance the dispersion of water droplets in the oil phase.

To confirm this, preliminary tests were conducted in the lab to examine the solubility of asphaltene in the separated maltenes from the oil sample. It was observed that the separated asphaltenes do not readily dissolve back in the maltene phase at room temperatures. At 60 ^{o}C, after 4 hours with the application of agitation, over 50% of asphaltene remained undissolved. Even at 100 ^{o}C (reservoir temperature) over 20% of the asphaltene remained undissolved in maltene phase after 4 hours of heating and agitation. This indicates that, if asphaltenes are separated from oil, they will not easily redissolve.

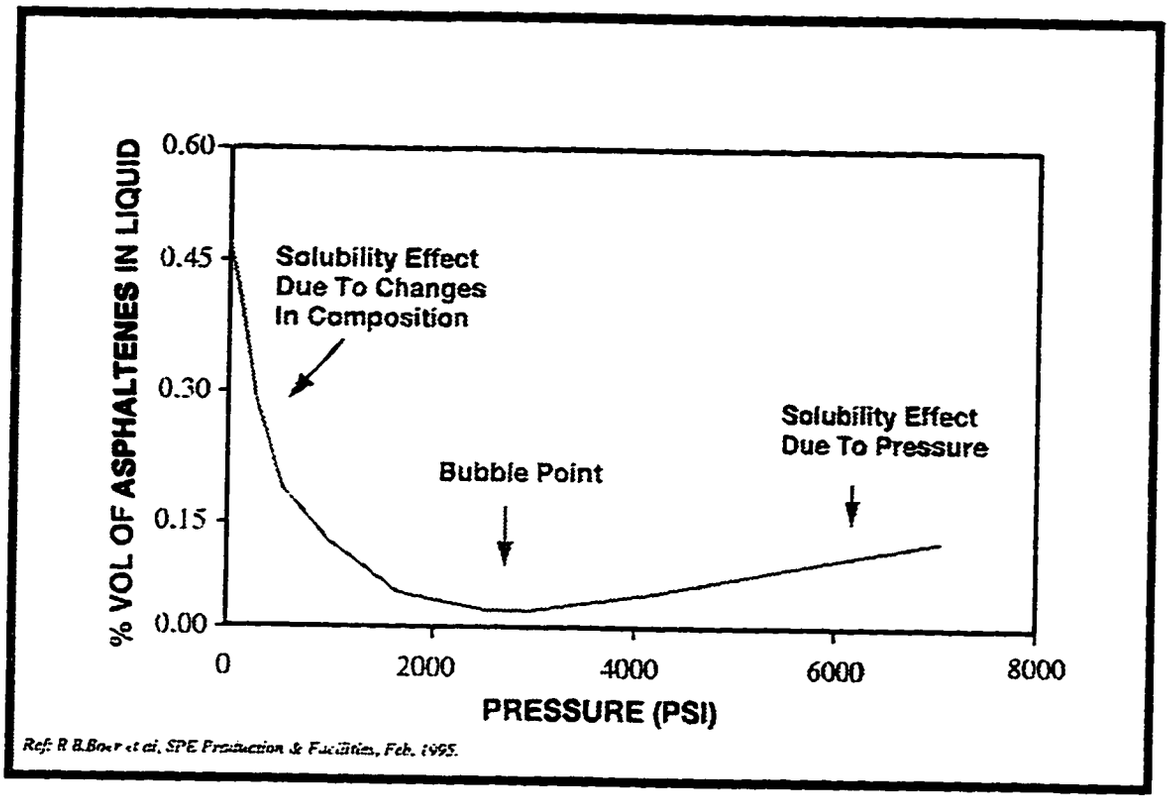


Figure 21. Asphaltene solubility as a function of pressure for a light crude.

4.12. EFFECT OF ASPHALTENES ON EMULSION FORMATION

To study the role of asphaltene on emulsion formation, Super Arab light crude was prepared with brine in the presence of 0, 3 and 6% additional asphaltene separated from Arab light crude at 80 degree C. The study indicated that 0% solution separated immediately and reached almost 80% of separated water within the first minutes. Whereas the 3% and 6% asphaltene separated within 3 and 20 minutes respectively (Figure 22).

4.13. INORGANIC AND ORGANIC SOLID INTERACTIONS:

Resin wetted surfaces were tested. It was observed that asphaltene covered surfaces present higher contact angles than resin covered surfaces (Figure 23). These fine particles ,with mixed wettability to oil and water, will collect at the water oil interface stabilizing water-oil emulsions. In addition, oil wetting wax particles can form during the production of oil. As long as they remain completely oil wet, they will remain in the oil phase. However if asphaltene aggregates adsorb on their surfaces this wettability will change from completely oil wetting to a mixed wetting. This occurs when hydrophobic side chains of asphaltene aggregates adsorb on a wax particle, producing a partially solvated particle. These solvated wax particles would then migrate to the oil-water interface contributing to the emulsion stability. In addition

as indicated in the literature, particle size of the solids is also important as it determines the equilibrium position of a particle at the interface.

Based on this literature data it is speculated that hydrophobic particles could contribute to the stability of water-in-oil emulsions produced from the field. To establish this view, tests were conducted and solids were separated from the produced emulsions from both problem and non-problem GOSPs as described below. Composition of these solids and particle size distributions were determined.

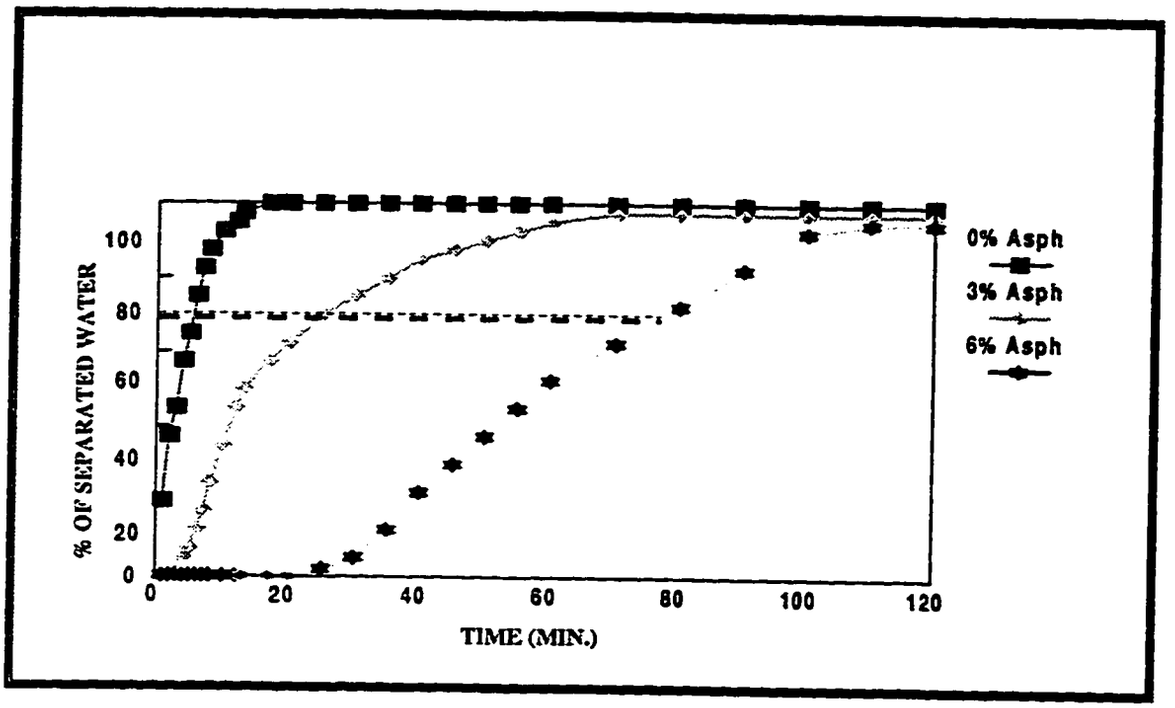


Figure 22. Effect of asphaltene on emulsion stability.

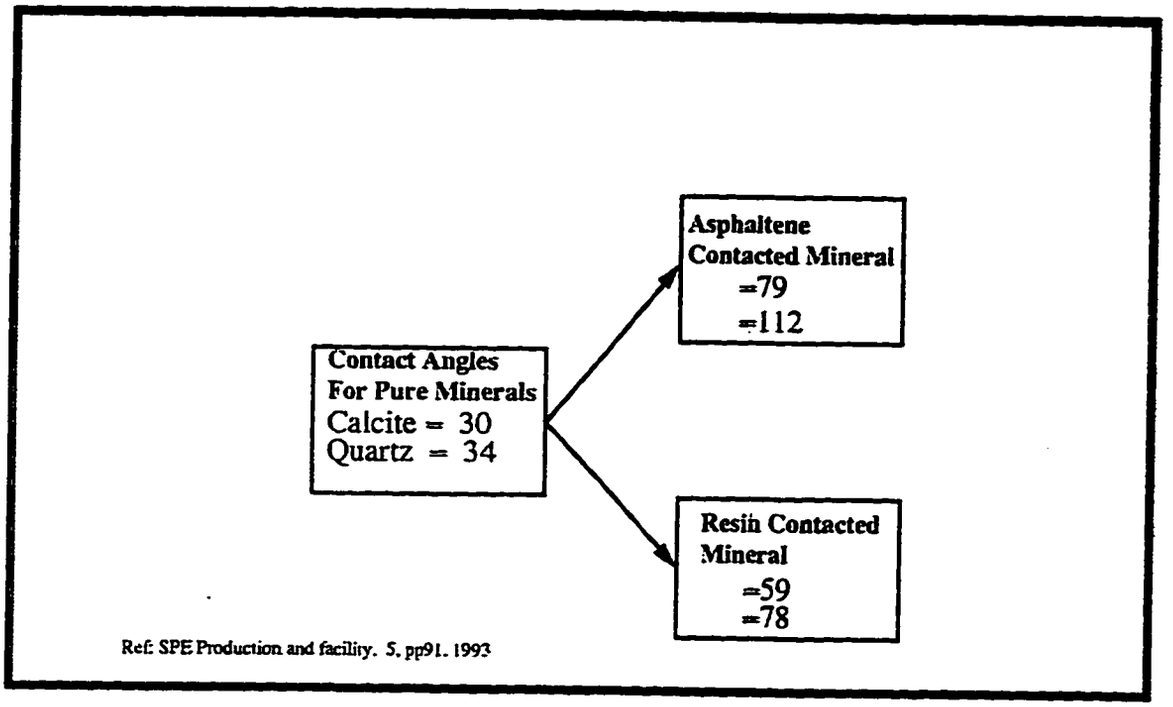


Figure 23. Equilibrium contact angles for pure minerals and for minerals with adsorbed oil polar fractions.

4.14. Wettability of Solids:

XRD and TGA data discussed earlier, have showed that the emulsion stabilizing solids separated from the field are composed of organic species (such as wax, asphaltene/resins which are hydrophobic in nature) and Inorganic species (mainly calcite particles). Further, these are completely mixed and covered with the other organic material such as partially resin solvated asphaltenes (Figure 28). The polar part of the oil, such as asphaltene/resin aggregates gets adsorbed on the surfaces of wax and other inorganic particles altering their wettability and increasing their emulsifying tendencies significantly. These solids together with asphaltene aggregates form a rigid layer around the water droplet, increasing the stability of the emulsion significantly. Stabilization processes of the water-in-oil emulsions by organic and inorganic solids are illustrated in Figures 24,25,26,27, and 28.

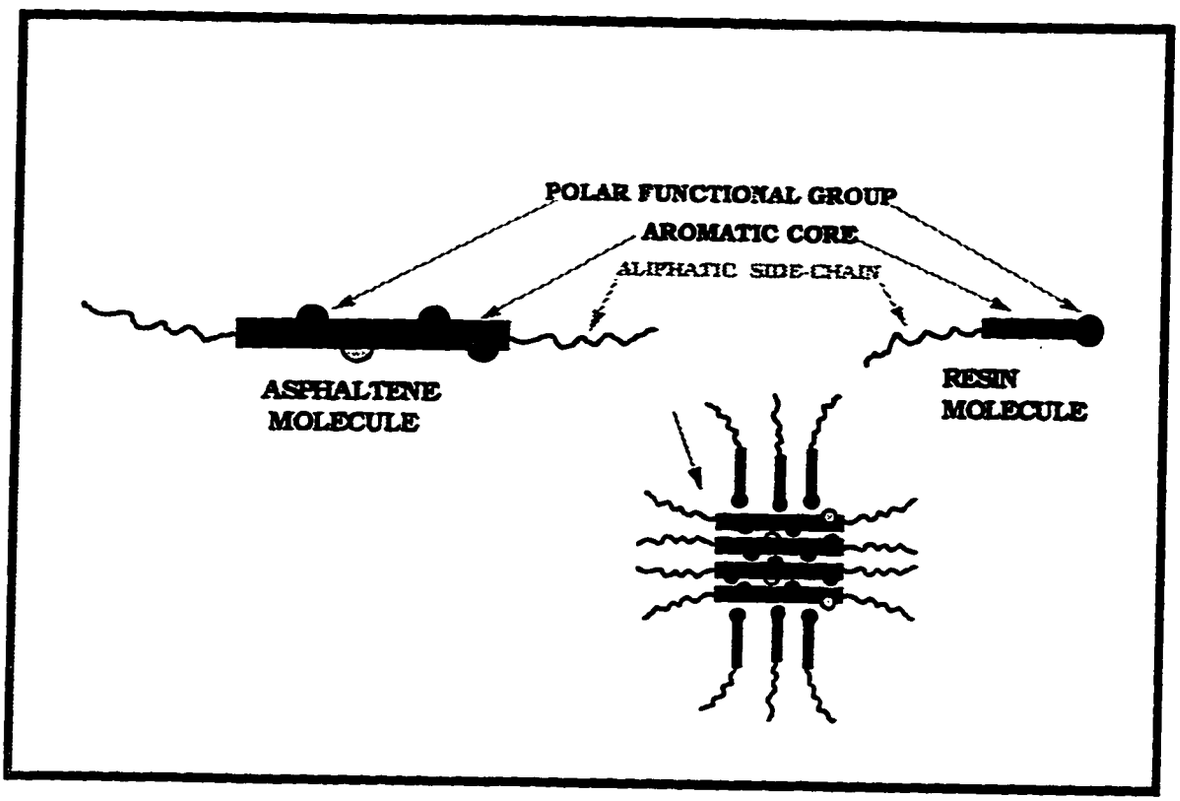
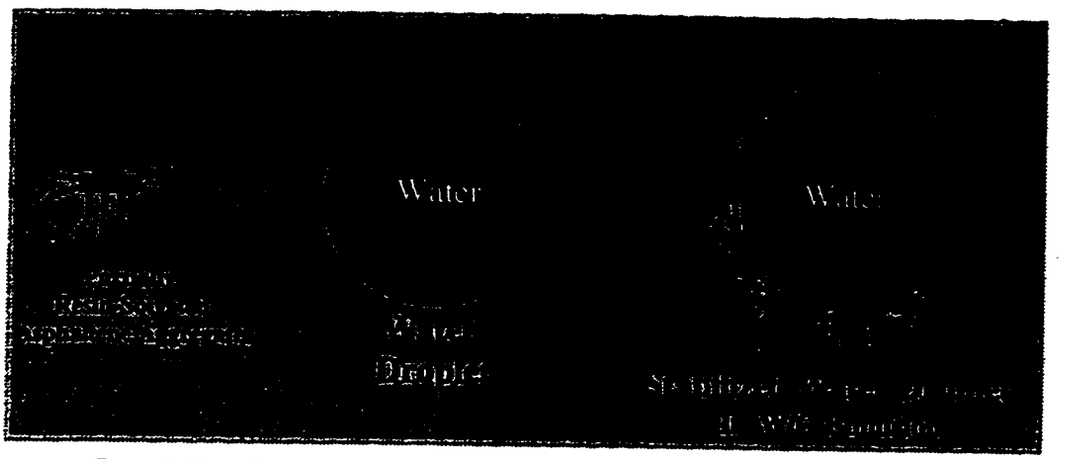
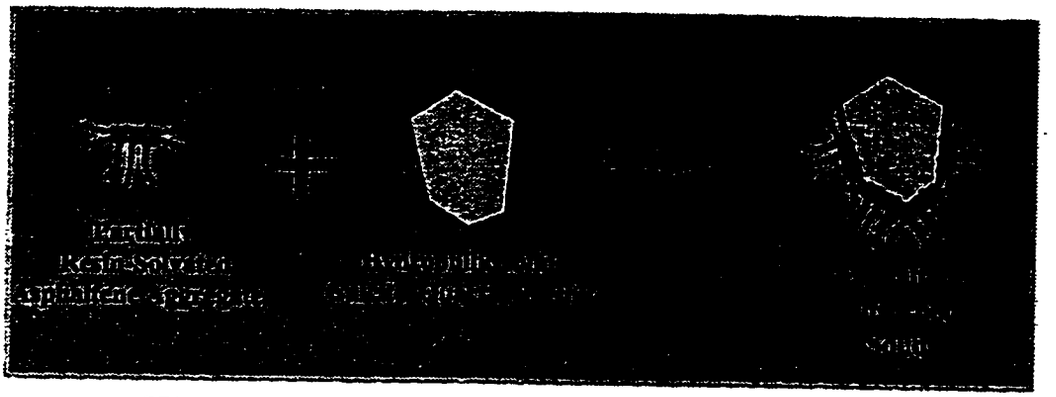


Figure 24. Asphaltene and resin molecules and their interaction.



Partially Resin-Solvated Asphaltene Aggregates Forming A Rigid Skin Layer Around the Water Droplets.

Figure 25. Stabilization of water droplets by resin/asphaltene aggregates.



Wettability of the Solids Changed From A Strong Hydrophilic to an Intermediate Wetting.

Figure 26. Adsorption of asphaltene/resin aggregates on hydrophilic solids

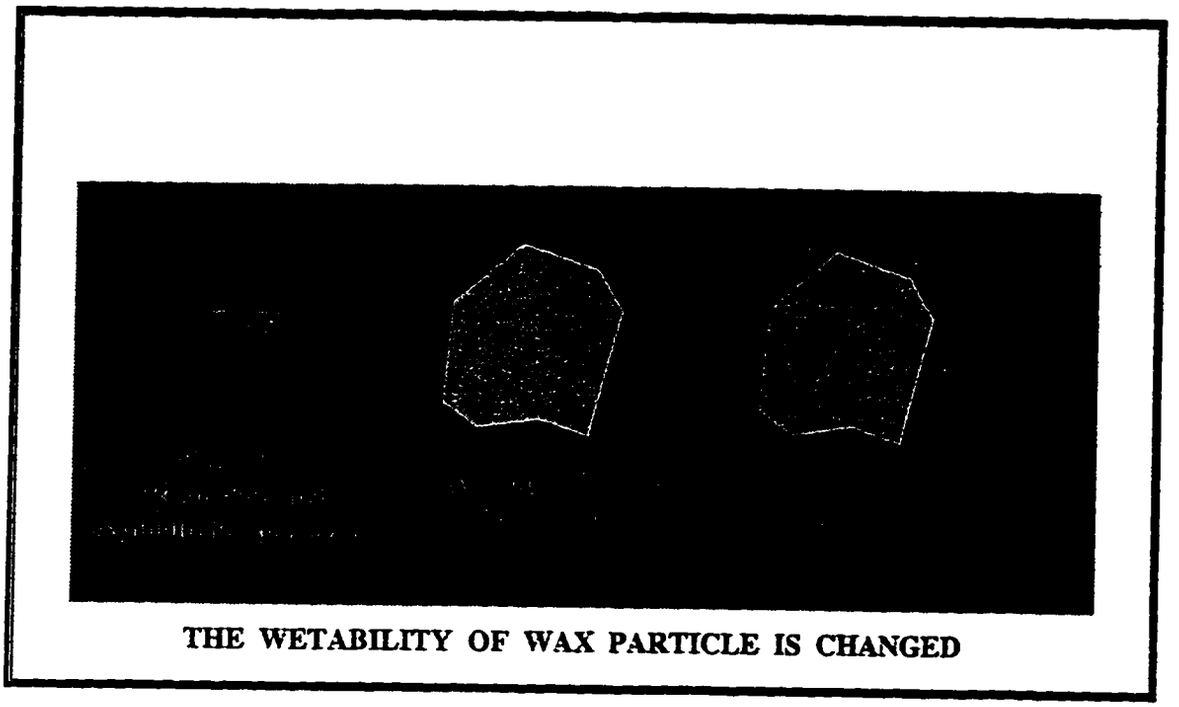


Figure 27. Adsorption of resin/asphaltene aggregates on wax particles.

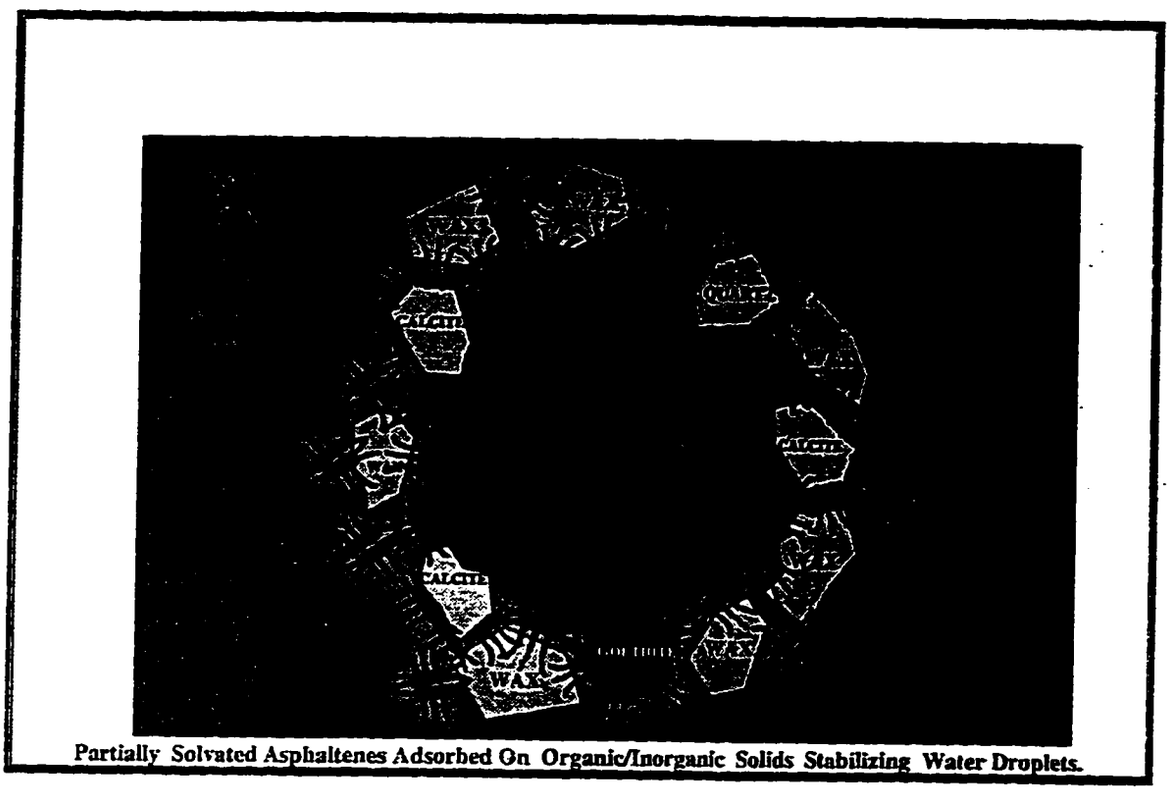


Figure 28. Stabilization of water-in-oil emulsions by organic and inorganic solids.

4.15. Particle Size Analysis of Solids

In addition to wettability, solid particle size plays an important role on the stability of emulsions. As the particle size decreases the surface area per unit mass of a given solid increases dramatically (as a cube of the particle radius). Subsequently more surface active material is adsorbed on the particles increasing their emulsion forming tendencies.

Tests were conducted on emulsion stabilizing solid samples separated from produced fluids from the field using a **Malvern Particle size analyzer.** These tests indicate that the emulsion stabilizing particles are very small, about 60% of the solid particles are below three microns in diameter as shown in Figure 29. As mentioned earlier these small particles will provide an appreciable surface area which will absorb surface active material such as asphaltenes/resins. This explains why the presence of a very insignificant amounts of solids (< 200 mg/L) can create stable tight emulsions.

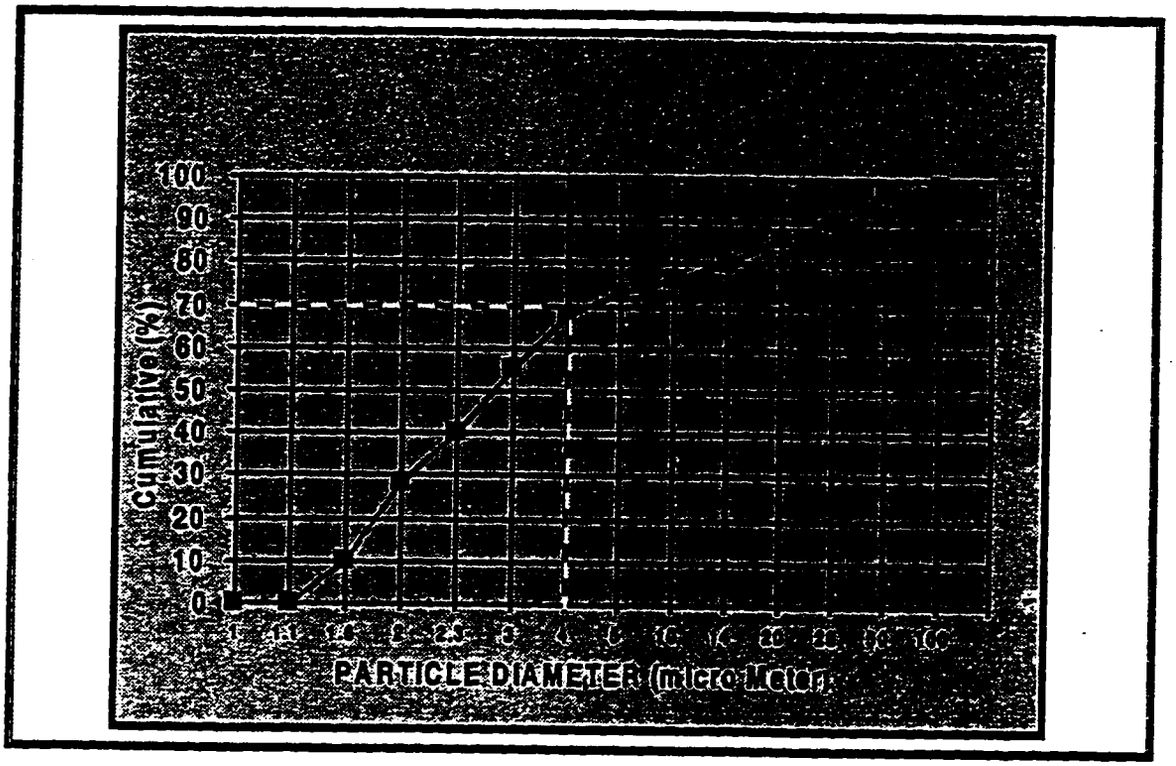


Figure 29. **Particle size analysis for solids separated from emulsion sample.**

4.16. CONTRIBUTION OF WAX CRYSTALS TO EMULSION STABILITY

Wax content of the solids separated from water-oil-interface of the emulsion sample from problem GOSP C is much higher than non-problem GOSP A&B indicating that wax crystals are contributing to tight emulsion formation.

The waxes found in crude oil are mixtures of different types of paraffin such normal paraffin, branched paraffin or isoparaffins and cycloparaffins Figure (30). It has been shown in the literature that, in production of some crude oils, wax crystals can play an important role on the formation of water-in-oil emulsions. Once wax crystals are formed, they can migrate to the oil-water- interface and contribute to the formation of rigid layers around water droplets. This will slow down the coalescence of colliding water droplets. However, this can occur if the polar molecules such as asphaltene and resin adsorb on the surface of wax crystals, and their wetability is altered from a complete oil-wet (hydrophobic) to an intermediate wetability. The alteration of wetability allows the wax

crystals to have affinity to aqueous phase. Some researchers also indicated that wax crystal also act in the bulk oil phase, where they inhibit film thinning between approaching droplets or by consuming the added demulsifier. It is likely that both of the above mechanism would contribute to stabilizing effect of wax on water-in-oil emulsions. Type of wax crystals and their crystalline nature as well as quantity of wax will play a key role on the way and how wax could interfere with oil-water separation process.

Normal paraffin wax molecules form a thin orthombic plates, some time long needles also form during their crystallization. Branched, isoparaffines and cycloparaffins will also form thin plate-like crystal, however their size will remain much smaller. This is due to steric hindrance effect of the side brunches and/or cyclic groups which restrict crystal growth forming microcystalline structure wax. These small wax crystals will possess a larger surface area which can contribute to emulsion stability at a greater extent than larger crystals resulting from normal paraffins.

Properties of paraffin as well as microcrystalline wax are both summarized in Table XI. This data show that microcrystalline wax has

different physical and chemical properties than paraffin wax. The melting point of paraffin waxes are in the range of 40 - 60°C, where as for microcrystalline waxes this is in the range of 60 - 90°C. Also the average molecular weights as well as the carbon number for microcrystalline waxes are both higher than n-paraffin waxes.

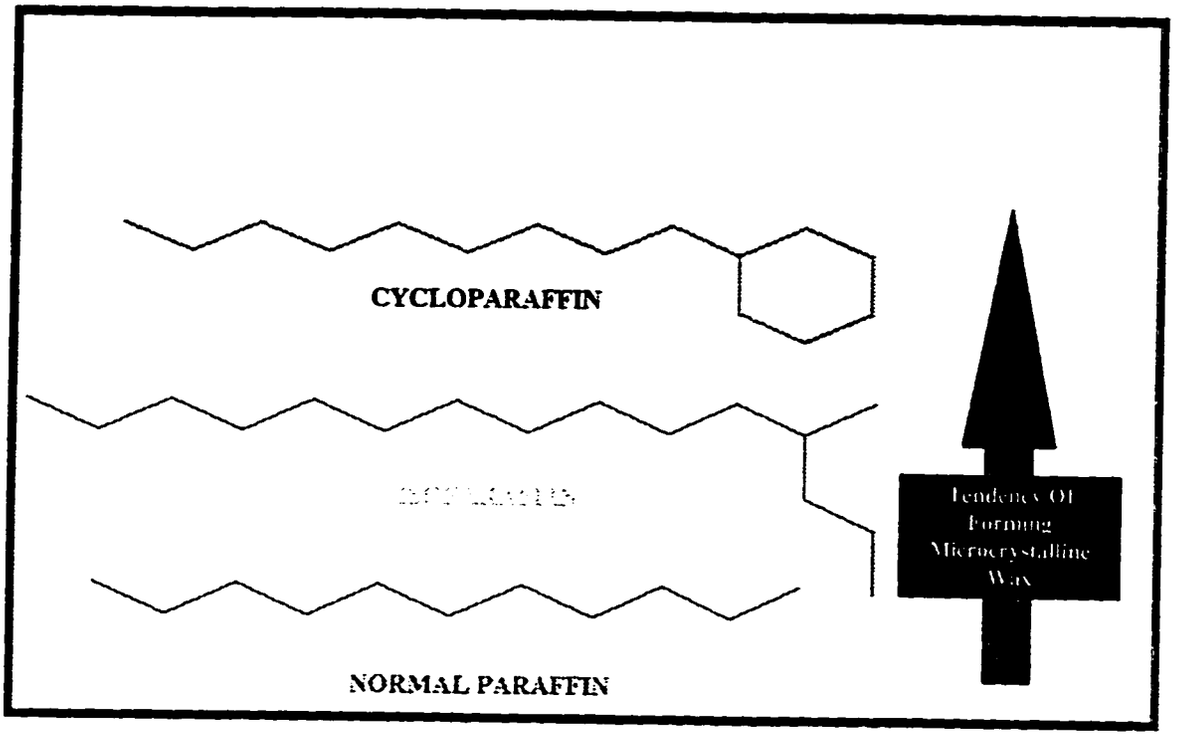


Figure 30. Petroleum waxes and their tendency to form microcrystalline structure.

TABLE XI

THE PROPERTIES OF PARAFFIN AND MICROCRYSTALLINE WAXES

TYPE	PARAFFIN WAXES	MICROCRYSTALLIN WAXES
Melting Point (° C)	40 - 60	60 - 90
Avg. Molecular Weight	300 - 450	400 - 800
Carbon Number	20 - 32	30 - 60

4.17. CHARACTERIZATION OF WAX CRYSTALS

Whole oil:	Non-problem well A
Oil separated by gravity:	Well B
Separated oil by heat and centrifuge:	Well B
Oil separated by gravity:	Well C
Separated oil by heat and centrifuge:	Well C

The wax content of these samples were about 2% by weight. The color of all these samples were dark brown, indicating that some asphaltene and resin molecules are associated with isolated wax crystals. Further recrystalization did not remove these associated impurities. However, by application of Column Chromatography all of these samples were purified. Initially colorless effluent was eluted from the column. This is hexane soluble which contained pure wax material. The remaining dark brown material was recovered from the column. The results of these

column chromatography separation procedures indicated that the amount of impurities present in all of the wax samples were under 10% by weight. Comparison of TGA analysis of Asphalted wax with unasphalted wax indicated that these impurities are asphaltene and resin (compare Figure 31 with Figure 32). TGA of de-asphalted wax crystals under the air has shown a sharp weight loss at temperatures of 200 - 300°C peaking at 279°C where as TGA for asphalted wax shows two additional peaks at 430 and 538°C(related to asphlatene and resins) in addition to the main peak at about 300°C which is related to wax material.

Molecular weights of all of these de-asphalted and asphalted wax samples were also determined by VPO and results are shown in Table XII. This table indicate that average molecular weight of all of the de-asphalted wax samples was less than the associated asphalted wax sample suggesting that asphalted wax crystals were associated with heavier fractions of oil (asphaltenes and resins). Therefore, based on TGA, VPO and Column Chromatographic separation test, it can be concluded that wax crystals adsorbed 5-10% of asphaltene and resins. This process alters their wetability and enables them to migrate to oil-water interface as described earlier.

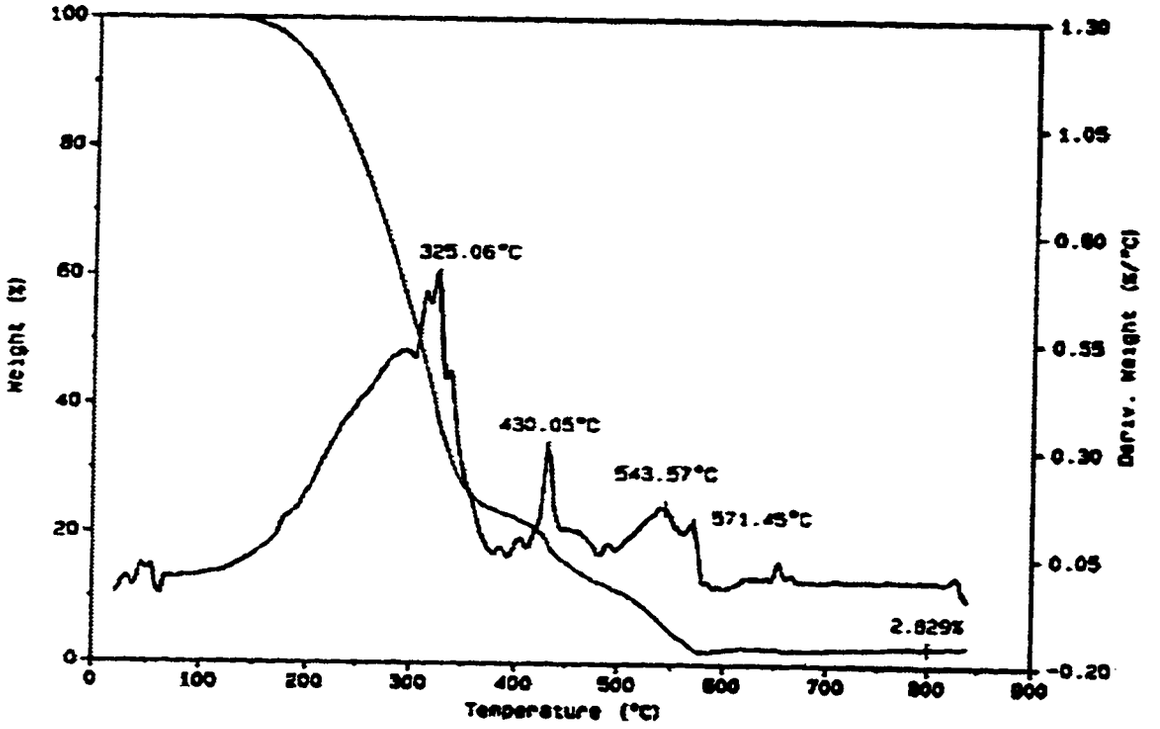


Figure 31. TGA of asphalted wax crystals under the air

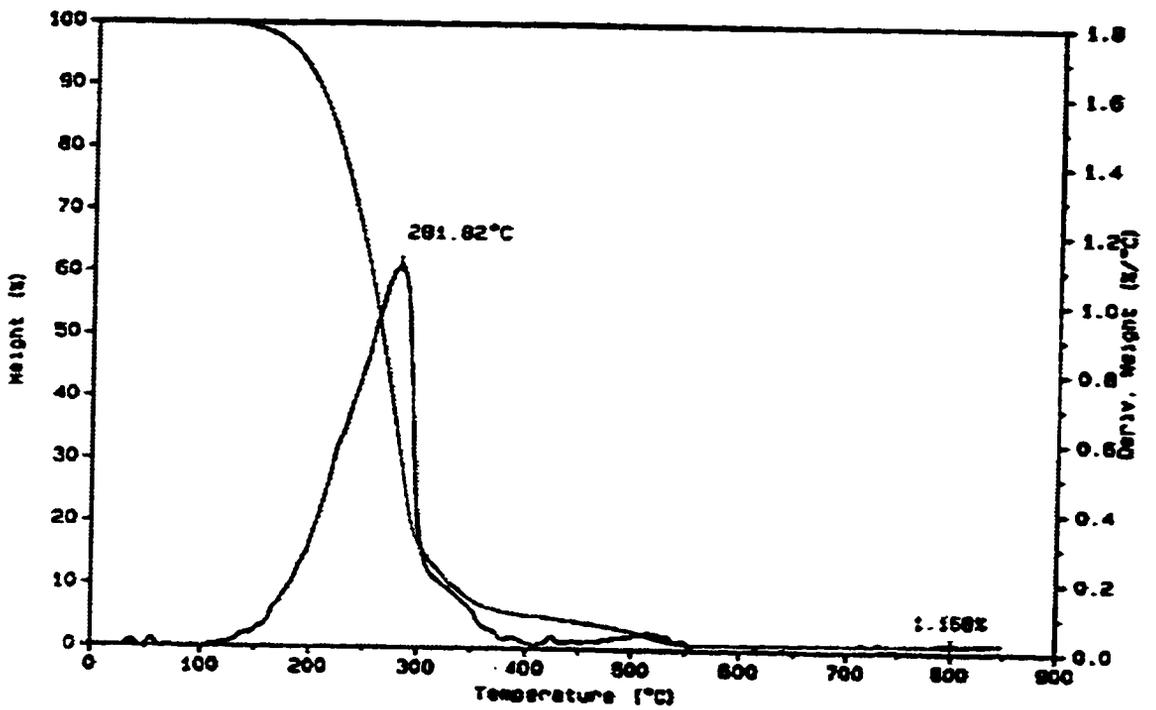


Figure 32: TGA of de-asphalted wax crystals under the air

TABLE XII

Interaction of Wax With Asphaltene And Resin

SAMPLE TYPE	AVERAGE MOLECULAR WEIGHT BY VPO	
	Deasphalted	Asphalted
WHOLE OIL (Well A)	460	511
FREE OIL (Well C)	421	443
EMULSIFIED OIL (Well C)	480	518
FREE OIL (Well B)	416	429
EMULSIFIED OIL (Well B)	513	536

Increased Average Molecular Weight of Wax Material Due To asphaltene/Resin Adsorption

4.18. SIMULATED DISTILLATION STUDY

Simulated Distillation was carried out for the wax samples listed above. The mid-boiling points for these samples were determined and listed in Tables (XIII) and (XIV). The data indicate that wax samples separated from free oil (separated by gravity) from both of the problem wells had lower boiling point than those derived from tight emulsion (by application of heat, centrifuge and demulsifier). The value of mid boiling point for whole oil from a non-problem well was between these two values. This indicates that wax for problem well and non-problem well are the same and during the emulsification process, heavier wax materials preferentially migrate, thus contributing to emulsion stability.

TABLE XIII

COMPARSION OF PROPERTIES OF WAX SAMPLE SEPARATED FROM PRODUCED FLUIDS FROM PROBLEM WELL-B AND NON-PROBLEM WELL-A

Sample Type	Mid-Boiling Point (° F) From Simu. Dist.	Average Molecular Weight	
		Simu. Dist.	VPO
Free Oil Separated By Gravity (Well B)	789	420	415
Separated Oil From Tight Emulsion (Well B)	867	507	513
Whole Oil From Non- Problem Well (A)	810	441	460

TABLE XIV

COMPARSION OF PROPERTIES OF WAX SAMPLE SEPARATED FROM PRODUCED FLUIDS FROM PROBLEM WELL-C AND NON-PROBLEM WELL-A

Sample Type	Mid-Boiling Point (° F) From Simu. Dist.	Average Molecular Weight	
		Simu. Dist.	VPO
Free Oil Separated By Gravity (Well C)	790	421	418
Separated Oil From Tight Emulsion (Well C)	845	480	498
Whole Oil From Non- Problem Well (A)	810	441	460

To verify this, HP-GPC was carried out for various oil samples separated by gravity as well as the associated samples obtained from tight emulsions (by heat, centrifuge and demulsifier addition) from two wells(B and C). The HP-GPC chromatogram for these samples are shown in Figures (33), (34) and (35). These figures indicate that, the oil separated from emulsions had smaller retention time than those obtained for the free oil samples. As the lower retention times in HP-GPC chromatograms are associated with large molecules, therefore, HP-GPC data confirms the other data described above indicating that tight emulsions contain heavier fractions. Also, the difference in retention times peaks increase as emulsion tightness increase. Produced fluids from wells (B) and (C) form tighter emulsion than well A and the associated retention time for these samples are also larger.

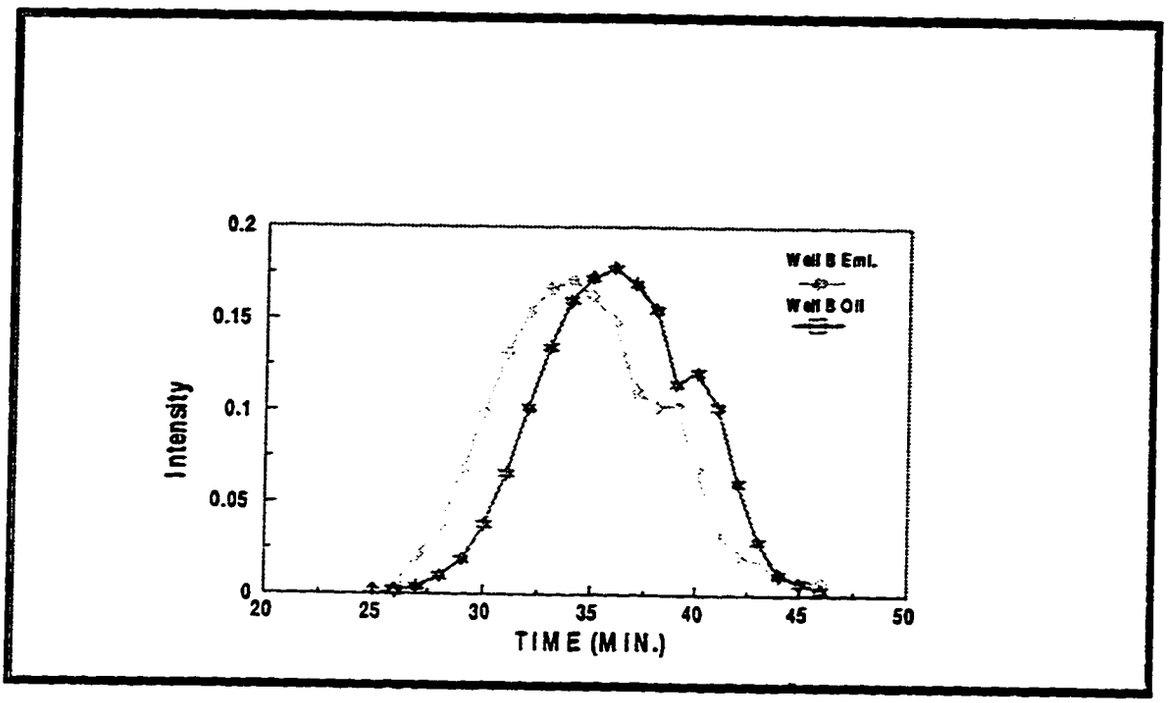


Figure 33. HP-GPC For asphaltene separated from tight emulsion

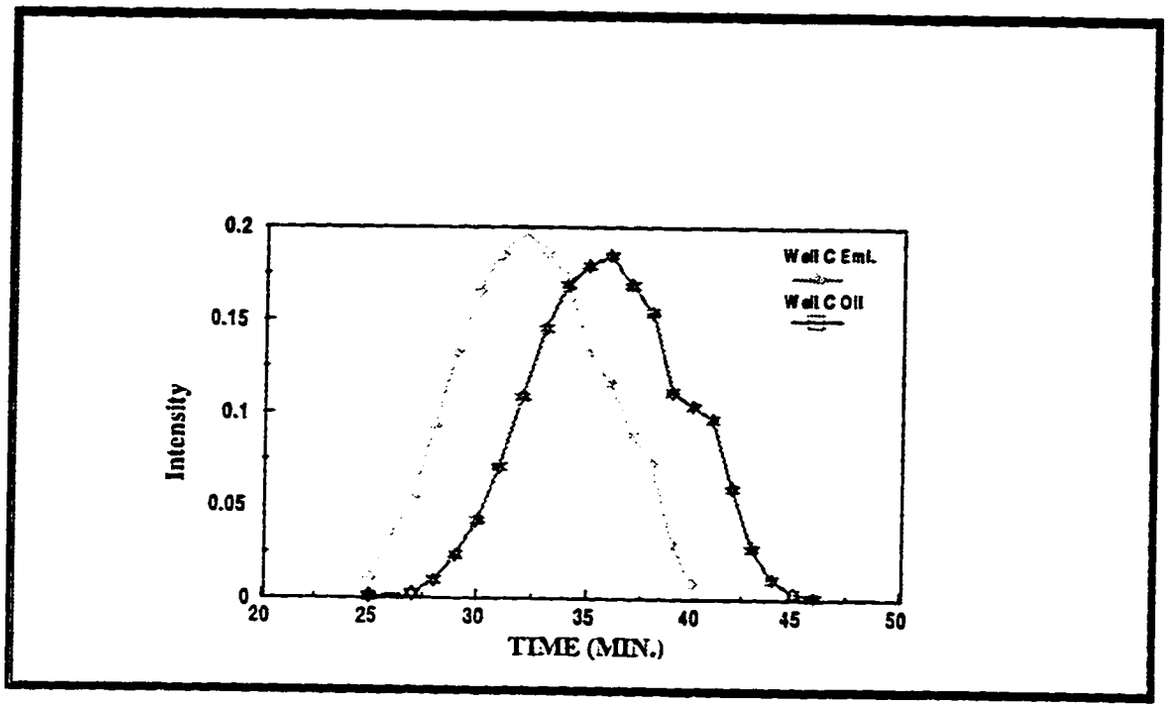


Figure 34. HP-GPC For asphaltene separated from tight emulsion

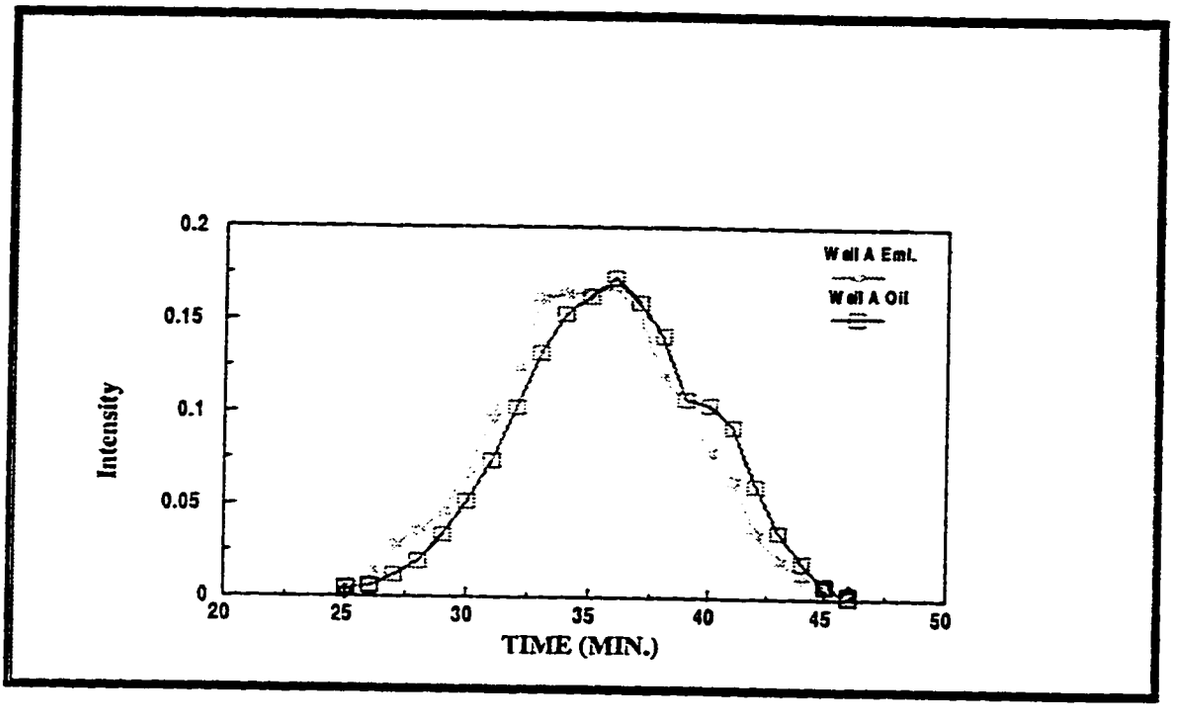


Figure 35. HP-GPC For asphaltene separated from loose emulsion

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are drawn from the present study:

- Calcite particles are causing tight emulsion formation.
- Tight emulsions have lower resin/asphaltene ratio than unstable emulsion.
- Microcrystalline wax particles are contributing to emulsion stability.
- Technique such as TGA, DSC, and HP-GPC are useful in understanding emulsion stability.
- The present study contributed significantly in understanding the mechanism of emulsion formation, and improved the emulsion model.
- Demulsifier concentrations needed to resolve tight emulsions are much greater than those used in normal GOSP operations.
- Tight emulsions have smaller droplets size distribution than unstable emulsions.
- Viscosity of tight emulsions are much greater than those of the associated oils.
- Temperature plays a key role on stability of tight emulsions

RECOMMENDATIONS

Minimize or avoid formation of tight emulsion by implementing one or more of the following methods depending on their feasibility:

- Apply scale inhibitor squeeze treatment.
- Alter demulsifier formulation by using organic dispersant.
- Prevent cooling produced fluids below 150°C by introducing heat or, insulating or burying flow lines.
- use crystal modifiers.
- Minimize choking production wells.

CHAPTER 6

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